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FORENSIC CHEMISTRY

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by

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PREFACE TO THE SECOND EDITION

In the light of further experience and of developments in the field of forensic chemistry considerable revision of the first edition of this book was desirable. This applies in particular to the sections on the examination of dusts and stains and to that dealing with the examination of toxic agents. These sections have, in fact, been almost entirely rewritten.

This was necessary because developments in the sphere of forensic chemistry emphasize the nature of its essential problem, namely, that of micro-chemical technique. In this field, also, considerable expansion has taken place not only in methods and technique, but in actual laboratory practice and use. It seemed natural, therefore, to lay an increased stress upon the principle and practice of these methods as they relate to the examination of materials likely to be submitted to the forensic chemical laboratory.

But it must equally be borne in mind that the technique of the examination of dusts, stains and related materials available in small amount is still in a comparatively rudimentary stage. Recently it has been authoritatively stated—and it is quite true—that the examination of dusts and related materials by the chemical methods described, or by any others, are often negative, and that the results of the examination must in any case be interpreted with great caution. This does not, however, absolve the investigator from the duty of carrying the investigation out, and using to that end every appropriate method at his disposal.

One of the new features of this second edition is a description of the method whereby the Stas-Otto principle of successive extraction can be applied to the examination of dusts and other material on a micro-scale. This does not mean that the Stas-Otto process can be formally so applied, or that the modification suggested can achieve that degree of precision associated with the process itself when it is used to isolate toxic materials from the body of a victim of poisoning. But it is a systematic process which can, and in practice often does serve, to identify compounds present in dust which are of evidential value. It is a qualitative not quantitative method of determination.

The author has been greatly helped in the revision by the suggestions made by colleagues, reviewers of the first edition, and other chemists. In particular he is indebted to Mr. D. B. Briggs who read the proofs and made many valuable suggestions. Mr. J. Guy was also good enough to check and correct the proofs. He hopes that the profit gained thereby is reflected in this new edition of *Forensic Chemistry*.

Richmond, Surrey.
June, 1946.

PREFACE TO THE FIRST EDITION

THE subject of forensic chemistry is one which does not figure largely in the chemical literature so that there would seem to be room for a text book on the subject. The special characteristic of this one is that the subject matter is strictly confined to formally chemical theory and technique.

The object has been first to collect together information now widely diffused throughout the criminological literature, and secondly, to outline the manner in which the practice of forensic chemistry is conducted in a forensic chemical laboratory.

The author has had practical experience of most of the operations described in this book and he has thus tried to produce not merely a theoretical treatise, but a practical guide for those engaged in forensic chemistry and for chemists who are called upon from time to time to undertake work of this character.

For much of the information supplied in this book the author as well as the reader is indebted to the many research workers who have carried out investigations in this field. It contains, also, a certain amount of material of which no complete account has yet appeared in the literature. A paper on the oxidation of ferrous iron in ink on paper, prepared for the Institute of Criminalistics has not yet been published in full by reason of interruption in publication of the *Revue Internationale de Criminalistique* owing to the war. A précis of the paper has, however, been published in this country in *Chemistry and Industry* by the courtesy of Dr. Stephen Miall the editor. The material appears for the first time in a text book here.

The author acknowledges the great help both direct and indirect which he has received from the workers named throughout the text and in the references in this book. And in particular he must allude to Dr. Edmond Locard, Director of the Institute of Criminalistics of the University of Lyon, and of the Laboratories of Technical Police, under whose direction he has worked, and to whom he owes such proficiency as he has in the theory and practice of forensic chemistry.

HENRY T. F. RHODES.

CONTENTS

PAGE

Preface to Second Edition v

Preface to First Edition v

PART ONE

APPLICATION OF CHEMICAL METHODS TO THE IDENTIFICATION OF THE PERSON

CHAPTER

I. Direct Identification of the Person 3–13

II. Indirect Identification of the Person 14–46

PART TWO

APPLICATION OF CHEMICAL METHODS TO THE PROOF OF *CORPUS DELICTI*

III. Stains 49–58

IV. Firearms and Explosives 59–72

V. The Chemical Examination of Questioned Documents 73–125

VI. The Chemical Examination of Counterfeit Money 126–134

VII. The Examination of Toxic Agents 135–156

References 157–160

Name Index 161

Subject Index 163

PART ONE

APPLICATION OF CHEMICAL METHODS TO THE IDENTIFICATION OF THE PERSON

CHAPTER I

DIRECT IDENTIFICATION OF THE PERSON

Skin Prints

As is well known, the discovery of the finger-print pattern as a means of identification of the person replaced the method of Bertillonage (measurement of the body). It has since been shown that other parts of the skin have characteristics which can be identified. Thus Locard (*Traité de Criminalistique*, *I.* 247) has found that the sweat pores of the fingers and palm are unique for the individual. Stirling (*Rev. Int. de Crim.* 350) has shown that the lines of the palmar surface are a means of identification. Claps (*Rev. Inter. de Crim.* 707) has studied impressions of the lips. Again, in an interesting note, Locard has reported that the lips of the vulva in females have a characteristic skin pattern. The spheres of identification of the human body have thus been considerably enlarged. Chemical or other methods of development are therefore applicable not only to the finger-print pattern but to skin impressions generally.

Development means the treatment of a skin impression by physical or chemical means. The object of the treatment is to make the latent print visible, or to define the details of it more clearly. Chemical methods of development have a restricted application, but they are important in their field.

Composition of Sweat

The skin impression is produced by the exudation from the sweat pores of the materials of perspiration. The composition of the sweat has been the subject of a number of investigations. Its composition has not been precisely determined. Classical analyses made by Favre and Harnack are not concordant, and indeed show gross variations.

ANALYSIS OF SWEAT

(Parts per 1,000)

Favre		*Harnack*	
Water	996·573	Water	990·9
Albuminoids	traces	Urea	1·2
Alkaline sudorates	1·562	Organic Matter	1·2
Urea	0·042	Sodium chloride	5·2
Alkaline lactates	0·317	Calcium phosphate	0·2
Fatty substances	0·013	Magnesium phosphate	0·1
Sodium chloride	2·230	Sulphates	0·6
Potassium chloride	0·024	Potassium carbonate	0·1
Alkaline sulphates	0·011		
Alkaline phosphates	traces		

Perspiration is, in fact, of very variable composition. Volatile fatty acids, traces of protein, perhaps urea (readily converted to ammonium carbonate), and fat appear, however, to be normal constituents of sweat. Sodium chloride is consistently present, and sulphates. The specific gravity varies from 1·001 to 1·010. Total solids from 4·4 to 22·6 (*Leung*, *Thèse de Lyon*, 1931, 11·0 to 14·7). Argutinski has found 1·24 to 1·61 of urea, but the presence of urea has not been confirmed by all investigators (Funke and others).

Types of Reaction in Development

The chemical development of skin impressions depends upon the presence of certain constituents which affect the reagents in definite ways. The reactions are mainly of three types: (1) Reagents such as iodine vapour are absorbed by the fat and fatty acids present in the deposit; (2) Reagents such as osmic acid which are reduced by substances to which they donate oxygen; (3) Reagents such as silver nitrate which react with inorganic chlorides to produce silver chloride which is subsequently reduced by a photo-chemical effect.

There are some special cases which should also be noted. A skin impression may be produced on a surface by a finger soiled with some foreign substance. It may then become of importance to determine the nature of the material producing the print for two reasons: (1) The nature of the stain may be an indirect clue to the identity of the depositor of it and (2) The print may be incompletely visible in detail and a knowledge of the material composing it may make development possible. An imperfectly visible stain made, for example, with potassium ferrocyanide would in regard to (1) suggest that it was associated with a chemical worker, and in regard to (2) would make its development possible with such a reagent as an aqueous solution of a ferric salt. In this way a mere smudge might be revealed as a finger or other skin print.

Surfaces on which Skin Prints are Found

The surfaces upon which skin prints may be found are very numerous. Polished surfaces of wood, metal, glass, or stone can retain the impressions. Paper also retains impressions, and it is upon this material that the true latent impressions are found. Prints upon paper are usually invisible until developed. It is thus particularly in connection with prints upon paper that chemical methods are used.

It is not, however, the case that paper is the only material which is amenable to chemical methods of development. The use of silver nitrate (*vide infra*) which has recently been developed is stated to have extended the range of materials upon which impressions can be sought.

They are said to include unpolished wood, and textile materials. It has not previously been possible to develop skin impressions upon these materials.

Prints upon Paper

The substances exuded by the sweat pores are absorbed by paper, the speed of absorption depending upon the quality and nature of the surface. In glazed and loaded papers the absorption is slow, and it is at its maximum upon uncoated paper and blotting paper. The development of the impression is correspondingly affected since the diffusion of the material by absorption results in the loss of the identity of the impression. Mitchell (*Documents and their Scientific Examination*) has stated that prints on highly-glazed paper can be developed after three years, highly-sized clayed paper retained impressions for several weeks ; tracing papers for three weeks, and ordinary unglazed paper such as is used for index cards for a few days only. For this reason it is essential that papers to be examined for fingerprints should be examined at the earliest possible stage in the enquiry.

Prints upon Wood

Two kinds of impressions have to be considered which are of an entirely different character. The print found upon polished wooden surfaces are generally best developed by mechanical methods. Unpolished wood, however, is not only chemically of the same nature as paper but in many respects physically comparable with it. Unpolished wood does not in all cases retain skin prints. If the surface is uneven no results can be obtained. Smooth wood is however also physically comparable with paper. The rate of absorption would appear to be slower than in the case of inferior paper. No complete investigation, however, has been made.

Reagents used in Practice

The chemical reagents most commonly used in practice for the development of prints are iodine, osmium tetroxide, and silver nitrate. It has not been conclusively shown that development of prints with any powder involves a chemical reaction of any importance. Their action is, in fact, of a physical type since the coloration of the print results from the mechanical adherence of the powder to the deposit, the powder being essentially unchanged chemically (*Rhodes*, *Rev. Inter. de Crim.* 1933, 328). It appears probable, however, that where metallic oxides, in particular oxides of the alkaline earths are used, a reaction may occur between the fatty acids of the print and the oxides. The greater efficiency of some powders appears not to depend only upon the particle size of the powder in question, and may be explained by a reaction of this kind.

METHODS OF DEVELOPMENT

ABSORPTION

Iodine.—Iodine or iodine vapour is absorbed by the fatty acid of which the print is partly composed. On exposing a finger or other skin print to this reagent it is accordingly coloured yellow or brown where the deposit is found. The paper is unchanged if the operation is carefully performed. Two methods can be used in practice. Stockis (*Arch. int. de med. leg. août*, 1912) deposits a thin layer of iodine by sublimation upon a sheet of celluloid. This prepared celluloid is then applied to the paper upon which the print is suspected to exist. In the hands of an experienced manipulator this method gives satisfactory results.

The application of the vapour of iodine is, however, more readily controlled. The classical method is to vapourize iodine with heat and to expose the paper to be tested to the vapours. Experience and skill in manipulation are necessary to obtain good results. If the process is not carefully carried out the whole surface of the paper becomes stained, so that the pattern of the print is destroyed. Iodine is, of course, fugitive, but it is not possible to repeat the developing process after the first charge of iodine has vapourized. The latent print will not absorb iodine a second time. The experiment will thus fail if these precautions are not observed.

Stockis (loc. cit.) has employed a method which utilizes iodine and aqueous vapours. A strong solution of iodine in potassium iodide is boiled in a shallow evaporating basin of large diameter. The paper is exposed in the same way as with the use of the dry vapour. Exposure must be rapid to avoid staining the paper, but latent prints are more sensitive to this treatment than to that with dry iodine vapour.

The Fixation of the Iodine Print

Iodine is generally recognized as the most satisfactory reagent for the development of skin prints on paper. One of its disadvantages is that the prints are difficult to photograph and they are, of course, fugitive. Popp. (*Fixierung von mit Iod sichbar gemachten Fingerspuren, Rev. Inter. de Crim., Nov.*, 1929, 492) has devised a method of fixation using palladium chloride. The reagent is prepared as follows:

Palladium chloride	0·10 gm.
Tannic acid	0·25 gm.
Alum	0·25 gm.
Hydrochloric acid (10%) . . .	0·5 cc.
Water	100·0 cc.

The developed print is treated with this solution, preferably in a developing dish, for slightly less than a minute. The paper is then thoroughly washed in a stream of water and dried. Under this treatment the developed print becomes dark brown and can readily be photographed.

Efficiency of the Method

The results obtained by development with iodine vary between wide limits. Variations in the composition of the deposit forming the print influence the result. It would appear probable that a deposit rich in fat and fatty acid would produce a more satisfactory result than one deficient in these constituents. Since it has been shown that the total solids of perspiration vary between wide limits the substances which absorb iodine must show a corresponding variation. On the other hand, no systematic investigation has been carried out under standardized experimental conditions.

REDUCTION

Osmium Tetroxide.—Charpy (1877) appears to have been the first to observe that the so-called osmic acid was coloured black by sweat. His method was applied to the development of finger-prints by Forgeot (1890). Locard (1906) also experimented with this reagent but with indifferent results. Ainsworth Mitchell, however (1920), has reported satisfactory results with the use of the vapour of an aqueous solution of osmium tetroxide.

Osmium tetroxide incorrectly described as osmic acid, the formula of which is H_2OsO_4, is a colourless crystalline compound which is reduced by organic matter to produce metallic osmium grey-black in colour. The colouration is permanent. Mitchell recommends the application of a 1 % aqueous solution of the reagent with a brush to the print to be developed. The paper is allowed to dry naturally. Sunlight hastens the reduction.

An alternative method is to boil a solution of osmium tetroxide and expose the surface with the print to be developed to the vapour. Care must be taken with this operation because of the irritant nature of the vapours.

Owing to the great readiness with which osmium tetroxide is reduced, this reagent tends to be too sensitive to produce well-defined results. The reaction can, however, be adjusted to develop prints showing sufficient detail. Mitchell has found that exposure of paper to the vapours of a boiling 1 % solution of osmium tetroxide produced prints full of fine detail. This method of development can therefore be recommended if careful attention is given to the manipulative details. It is in general true, however, that this method is more difficult to control than that of iodine absorption.

Ruthenium Tetroxide.—This substance exists in the form of yellow crystals. It differs from osmium tetroxide in being only slightly soluble in water and it is less stable. Its behaviour in the presence of organic matter resembles that of osmium tetroxide, that is to say that it produces a black compound. The reaction taking place is not precisely known, but it appears probable that the tetroxide is reduced to the hemitrioxide Ru_2O_3.

In practice the best results for the development of skin prints are obtained by heating the crystals over a water bath at a temperature not exceeding 50°C. The heating must not be too rapid, nor the temperature raised too high or an explosion may occur. The tetroxide is decomposed at 100°C. at atmospheric pressure. In the writer's experience satisfactory results are not obtained by heating an aqueous solution of ruthenium tetroxide. First, the slight solubility of the oxide reduces the utility of the method, and secondly, the tetroxide is decomposed at boiling point so that it does not reach the organic material of the skin print in this form. Since it is the tetroxide itself which reacts most energetically with organic matter, it seems important that the operation should be controlled in such a way as to ensure that the reaction is actually one between the tetroxide and the organic matter.

PHOTO-CHEMICAL METHODS OF DEVELOPMENT

Silver Nitrate.—The reaction involved in the development of skin prints with silver nitrate is of an entirely different kind. The sodium chloride present in all perspiration marks reacts with the silver nitrate to form silver chloride. The reaction, of course, takes place at the surfaces corresponding to the ridges of the print, so that a film of silver chloride is produced in accordance with the pattern of the skin print.

This method of development is extremely sensitive because of the relatively high concentration of sodium chloride present in all types of perspiration. Further, the reduction of minute quantities of silver chloride produce a pronounced black stain. For this reason silver nitrate development is more sensitive a method than any of those previously described.

It is commonly stated that silver nitrate development is a recently devised method of developing skin prints. It is, however, an interesting fact that Aubert, a French surgeon, was the first to draw attention to the reaction between silver nitrate and perspiration products in 1878, some years before finger-prints were generally recognized as a means of identification of the person. Aubert was studying the reaction of the sweat glands and found that their products reacted with silver nitrate to produce silver chloride which upon reduction became visible as a black stain. The classic work of Forgeot in 1891 was concerned with the use of silver nitrate as a reagent for the development of finger-prints. Essentially his method does not differ from that used at present. He recognized the nature of the reaction as being one which involved the formation of silver chloride, the subsequent development being due to a photo-chemical effect upon the silver chloride. The nature of the latter reaction was, however, not well understood at that time, so that Forgeot's method was rudimentary (*vide infra*).

Silver nitrate can be used to develop skin impressions upon a variety of surfaces of which paper is the most satisfactory. The original deposit of sodium chloride, however, has been shown to retain the pattern corresponding to the skin print upon unpolished wood, and also, it is claimed, upon textile fabrics. This is of great importance forensically because theoretically at least skin impressions can be developed upon the inner surface of gloves, upon handkerchiefs, and other fabrics. It will also be recalled that in the Hauptmann trial in America, prints upon a step ladder were made visible in this way. By reason of the rapid diffusion of substances of fatty origin upon textile fabrics and also apparently upon unpolished wood, it is not possible to develop skin impressions on these materials by the methods previously described. Where the medium to be developed is sodium chloride, the case is different. Sodium chloride undergoes diffusion, but at a much slower rate than fatty materials. The reason for this is not clearly understood since it might be expected that the great solubility of sodium chloride would result in rapid diffusion where much moisture was present in the material with which it was incorporated. In the case of skin prints, however, there would appear to be present substances which retard its migration. This substratum of sodium chloride is thus particularly amenable to development in a variety of circumstances and under some conditions for long periods after the impressions have been made.

Method of Development with Silver Nitrate

An aqueous solution of silver nitrate of about, and not in excess of, 5% should be used. If the surface upon which the print is to be developed is of suitable size, the most satisfactory method of treating it is immersion in a photographic developing dish. This operation must be performed in darkness or at least in diffused light to avoid photo-chemical reduction of the silver nitrate. The treatment should continue for about five minutes.

The treated surface must then be washed in running water until the washing gives no reaction for the silver ion with a chloride. It is essential that this washing should be thorough, and it should be carried out in diffused light.

At this stage that part of the surface corresponding to the skin pattern is coated with silver chloride. It remains to reduce the silver chloride when the pattern will appear in black.

Forgeot's method was simply to expose the surface to the light. When the print had attained maximum intensity it was treated with sodium thiosulphate. The results, however, were not always consistent nor completely satisfactory. It was then generally agreed that the photo-chemical reaction resulted in a reduction which produced the sub-chloride Ag_2Cl. It was assumed that " fixation " with sodium thiosulphate reduced the sub-chloride to metallic silver and removed silver chloride. Forgeot used the method to " fix " the print, but found that it sometimes reduced its intensity. That a sub-chloride of silver is formed in these circumstances is not now generally accepted so that the only certain result of this treatment was the removal of excess silver chloride.

Reduction of the Silver Chloride

A more recent and satisfactory method is energetically to reduce the silver chloride with a photographic developer. The disadvantage of utilizing the photo-chemical effect is that the reaction is not completely understood, and is thought by some authorities to leave a considerable proportion of the silver chloride unchanged. This may account for the inconsistent and unsatisfactory results obtained by Forgeot. In any case experiment has shown that a more pronounced colouration is produced by reduction with a developer. The present writer has found the solutions recommended by Locard (*Traité de Criminalistique* II, 864) for the development of spermatozoa stained with silver nitrate very suitable as a reducing agent. They are prepared as follows :

Water . . .	100 parts	or	Water . .	100 parts
Formaldehyde . .	5		Hydroquinone .	1·6
Pyrogallic acid . .	4		Sodium sulphite .	10
Pyridine . . .	8		Pyridine . .	8

The former of these is, in our view, the more efficient.

This operation should also be carried out in diffused light to prevent photo-chemical interference. The development should be continued until the maximum intensity has been attained. The print should finally be washed and dried.

Modification of the Process

Very satisfactory results can be obtained by this method if these precautions are carefully observed. In many cases it is not practicable to immerse the object in a developing dish. If this cannot be done, the silver nitrate must be painted on to the surface. The technique of washing a surface which cannot be completely immersed is also more difficult than in the example cited. It is, however, equally necessary to ensure that the silver nitrate is completely removed from the treated surface before the reduction is attempted. Development of the print must also be effected by application of the developer with a brush. The developed print must then be washed in running water.

Method of Finn and Cornish

Finn and Cornish have reported (*Ind. Eng. Chem. News Ed., Feb.*, 1935, 73, 75) interesting results of development of prints on paper with silver nitrate. They recommend the use of an 0·2% solution of the salt. The material to be developed is soaked for two hours in the silver nitrate bath and is then thoroughly washed. The paper is then dried and developed with a solution of the M.G. type or with a mixture of sodium carbonate and formaldehyde. It is again washed and fixed with a solution of sodium thiosulphate.

These authors make some interesting observations concerning the migration of chloride ions of sweat under varying conditions of humidity and temperature. (*See also Bieger and Diesselhorst, Deut. Med. Wochshr.* 29, 1903.) They suggest that, in fact, the age of the print can be approximately estimated by the sharpness of the print which, of course, depends upon the diffusion of the chloride. The authors, however, emphasize that extreme caution is necessary in interpreting the results. It is, however, always a fair inference that if diffusion has taken place to an extent which makes the pattern of the print unrecognizable, its origin is not recent.

Method of E. M. Hudson

Dr. Hudson, director of the Technical Laboratory of Police of the city of New York, recommends the use of a 10% solution of silver nitrate which has been acidified with acetic acid. In the alternative the surface to be developed may be treated with a 10% solution of acetic acid after treatment with silver nitrate. In other respects the process follows those described with the distinction that photo-chemical means are used for development. Hudson recommends the use of sunlight or preferably ultra-violet light. The print is finally " fixed " with sodium thiosulphate.

The presence of acetic acid decomposes carbonates and other substances which, if present, might interfere with the silver chloride reaction. The present writer has not found that the reaction in acid solution differs from the neutral reaction, but there can be no objection to acidification and it is correct on theoretical grounds.

Dr. Hudson has obtained remarkable results from prints upon handkerchiefs, collars, and other textiles. The method is also applicable to the treatment of latent prints upon wood. But both on theoretical grounds and in the experience of the present writer development of the print with a reducing agent is preferable to photo-chemical development.

Applications

Development with silver nitrate has greatly increased the scope of the chemical development of skin prints. Chemical methods, formerly seldom employed except for the development of skin prints on paper, are now by reason of this new technique applicable to wood, textiles, and other materials upon which prints could not be developed. It is extremely sensitive and this is in certain circumstances one of its disadvantages. Minute traces of chloride upon the surface carrying the print prevent the successful application of the method. The variable diffusion rate of the chloride ions under different conditions of temperature and humidity also drastically influence the result. In circumstances quite frequently met with, the identity of the print may have disappeared in twenty-four hours.

The method has, however, been applied to the development of prints on the inside of gloves, upon wooden instruments such as ladders, and the unpolished handles of tools or weapons after considerable periods of time. There is no objection as a rule to its experimental use since the method, except in the case of paper, is only applicable where other methods would be useless. In regard to paper it has been clearly shown that if the print can be developed at all, silver nitrate is in all cases a suitable reagent, and in many cases superior to others.

PRINTS PRODUCED BY FOREIGN MATERIALS

Skin prints formed by materials other than sweat are sometimes amenable to chemical development. If latent, however, the material forming them cannot be identified. If, however, a coloured stain suspected to be a skin print is observed, an attempt should be made to ascertain its composition. In many cases whilst the print may be visible it is not sufficiently distinct to ascertain its pattern. Development then becomes necessary. A micro-chemical examination of a small area of the print using Grey's reagents (*vide infra* p. 17) may result in its identification. The colour may also be of assistance. Thus a yellow stain might be one of potassium ferrocyanide, one of blue a copper salt, or a brown stain an oxidized iron salt. If the composition can be ascertained development consists in treatment with a reagent which produces a highly-coloured or black compound. Since a high percentage of metallic sulphides is black, H_2S water, or ammonium sulphide are reagents likely to be effective for development.

If, however, the nature of the stain cannot be ascertained, it is preferable to resort to exposure to iodine vapour. Iodine will often mechanically adhere to the material producing the stain and thus reveal the details of its pattern.

CHAPTER II

INDIRECT IDENTIFICATION OF THE PERSON

Strictly the identification of the person means a definition of those characteristics which distinguish him from all other persons.

Locard (*Traité de Criminalistique*, *III*, *I*, 8) has said :

> Au sens précis, l'identité est la qualité d'une chose qui fait qu'elle est elle-même et se différencie de toute autre. C'est, en mathématiques, le fait qu'un terme (valeur, courbe, symbole algébrique) représente la même idée qu'un autre et se confond avec lui, avec, comme formule type, l'équation :
>
> $$O = O$$
>
> C'est, en logique, l'enveloppement en un même concept de deux entités, dont la comparaison demeure ainsi tautologique, suivant le principe d'identité: *quod est est*, ou le principe de contradiction : *quod non est non est*. C'est enfin, en criminalistique et en droit l'ensemble des caractères par lesquels un homme définit sa personnalité propre et se distingue de tout autre. Dans ce dernier ordre d'idées, établir l'identité d'un individu, est l'opération judiciaire ou médiocolégale appelée identification.

The last two sentences in this excellent definition to some extent justify our use of the term indirect identification. It is necessary to distinguish between those factors like finger and skin prints which are in themselves completely descriptive of the identity of the person, and those which are of themselves incompletely descriptive but which contribute in varying degrees to identification.

OCCUPATIONAL DUST

An example is the so-called occupational dust with which we shall first deal. Hans Gross (*Criminal Investigation*) quotes a case of the discovery of glue and minute fragments of wood in clothing. The inference was that the owner of the coat was a cabinet maker, a conclusion which was afterwards confirmed. This is an example of indirect and partial identification. Such an observation does not serve to distinguish the wearer of the coat from all other persons, but it places him in an identifiable class and thus serves to distinguish him from the great majority of other persons. From the forensic chemical point of view, the identification of materials of this type is of great importance.

Classification of Dusts

The classical work of Locard, Popp, Icard, and others has resulted in a classification of occupational dusts which is of the greatest importance in criminalistics. The general classification divides them into organic and inorganic dusts, the particular classification into those associated with a given occupation or occupations. Theoretically, of course, all dusts are amenable to chemical examination, but in practice only certain dusts are identifiable by chemical methods.

Among the dusts classified as those of occupation (*Locard*, *Traité de Criminalistique*, *II*, 843–846) may be mentioned coal dust, starch, metallic oxides and metallic powders, calcium sulphate (gypsum), drugs and related compounds, sugar, and dyes. These are materials of a type which can be examined chemically and in many cases positively identified. It is not, of course, possible to deal with the technique to be followed in every case, but only to describe the scheme which must be followed in the analysis of dust.

The Collection of Dust

The classical method of collecting dust from clothing or other material was to enclose it in a strong bag of brown paper which was then beaten and the dust collected. This method has now been replaced by the use of a special vacuum cleaner designed by Söderman (*Rev. Inter. de Chem.*, 373, 1931). Essentially the apparatus does not differ from the ordinary vacuum cleaner. It is, however, fitted with three filters with screens of different mesh. This triple screening is of great value since it secures a differential sampling of the dust in terms of particle size.

By the use of nozzles of different sizes it is possible to regulate the suction according to the material from which dust is to be extracted. It has not been found possible to extract dust from material more closely woven than silk. For cotton materials and for flannel less suction is required ; from the extraction of dust from pockets a very light suction should be used.

OTHER SOURCES OF OCCUPATIONAL DUST

Dusts are also found in the hair including the hair of the eyebrows and in the wax of the ears.

Hair.—No special method has been devised for the removal of dust from the hair. A brush must on no account be used owing to its tendency to retain dust in general or dusts of a particular type more readily than others. The most convenient instrument is a hair comb, care being taken when using it to avoid contact with the epidermis or epithelium as far as possible.

Ears.—Great care is necessary in removing wax from the ears or the ear-drum may be injured. It is advisable to request the services of a medical man who is able to remove a much larger quantity of wax with less danger of injury to the subject. It is important that as much wax as possible should be removed since dusts deeply imbedded in the wax may be equally or even more important from an evidential point of view than those found at the surface.

THE PRELIMINARY TREATMENT OF DUST

Extracted Dusts.—In no case must this preliminary type of examination be undertaken unless quantities of the order of 100–200 mgm. of material are available. Where smaller quantities are involved the strictly micro-chemical methods described (*infra* p. 20) must be used. It is not proposed to deal with the microscopic examination as such. An examination should, however, be made with a lens with which it may be possible to detect the presence of crystals, coloured substances not recognizable with the naked eye, and other substances which may have some characteristic appearance. Whilst it is never possible to arrive at a positive decision by means of an examination of this kind, it may be a useful guide in the subsequent investigation.

Every precaution must be taken to conserve the material examined. The quantity of dust available seldom exceeds 0·5 gm. in the case of clothing. In many instances, the quantity available will be of the order of milligrammes. If, however, sufficient dust is available the following preliminary tests should be made. (1) A small quantity should be treated with a drop of water upon a cupped spotting tile ; (2) A second lot should be treated with one drop of 0·1 N HCl and (3) A drop of ethyl alcohol should be applied to a third quantity.

(1) All examinations must be made with a lens. (*a*) The colour, if any, of the aqueous drop should be noted. (*b*) It should be noted what proportion of the solid matter remains in suspension, and what proportion settles rapidly. (*c*) A minute quantity of the aqueous drop should be drawn up with a fine capillary and transferred to sensitive neutral litmus paper. The reaction acid, alkaline, or neutral must be noted.

(2) (*a*) When the drop of acid is added which must be delivered very cautiously from a fine capillary, the reaction, if any, must be noted. (*b*) Bubbles of gas may be evolved or (*c*) a precipitate formed. (*d*) Any change in colour in the drop must be noted. (*e*) Material dissolved by the acid must be noted.

(3) (*a*) The colour of the alcoholic drop must be noted. (*b*) It must be compared with the colour of drops (1) and (2). (*c*) Any other change such as the quantity of solid matter dissolved must be noted.

(4) A further small portion of the dust should be ignited. This operation should not be done in a crucible but on a thin disc of porcelain.

The colour and other characteristics of the residue are more readily perceptible if this method of incineration is used. (*a*) The smell on ignition should be carefully noted. (*b*) The colour of the ash must be observed.

Spectroscopic examination is not within the scope of this book. It should be noted, however, in connection with the ignition of dust that a spectroscopic examination can be made and in many cases is very useful. The reader is, however, referred to the appropriate literature (*S. Judd Lewis*, *Analyst*, 60 (1935), 10–17).

The Chemical Examination of Dust

It is important to observe first, that a quantitative examination of dust is seldom practicable, and if practicable is of little use except in special cases. (*vide supra.*) From a criminalistic point of view the identification of the substances present is sufficient. Secondly, substances present in dust cannot, of course, readily be identified as such. In regard to inorganic constituents bases and acid radicles can be recognized. Organic compounds can also in some cases be identified as such. The nature of dusts, however, requires the application of special methods in particular cases. It is not possible to deal with special cases in detail. A systematic scheme of procedure should, however, be followed whenever the quantity of material makes it possible. In the micro-chemical examination of dust, as in other micro-chemical operations, the procedure depends upon the quantity of material available.

DETECTION OF COMMON METALS

Micro-chemical methods devised by Grey (*Practical Chemistry by Micro-methods*, *Cambridge*, 1925) can be used for the detection of metals. Three drops of the ash of the dust which has been brought into solution are treated with drops of ammonium carbonate, potassium iodide, and ammonium sulphide. The reactions appear in the table given on the opposite page.

In the author's experience this scheme of analysis is of great value in many cases. The test is simple to apply and rapid. Since it can be applied to a very small quantity of the substance to be tested it is always useful as a preliminary test.

The tests may give confusing results where more than one metal is present, but this is not always the case. It frequently happens that in occupational dusts a particular metal is present in considerable excess of other bases. In these circumstances the reaction given by this metal may mask that of others and thus make the test specific.

On the other hand, where the concentration of the metallic constituent is feeble the results must be interpreted with great caution. The reaction of manganese, cadmium, and arsenic can be confused if feeble. Chromium and iron may also give colour reactions which are difficult to distinguish in weak concentration. Further certain mixtures of metals may give colour reactions which appear to indicate the presence of a single metal which is not in fact a constituent of the mixture.

MICRO-CHEMICAL REACTIONS OF THE COMMON METALS

(E. C. Grey. *Practical Chemistry by Micro-Methods.*)

	Ammonium Carbonate	Ammonium Sulphide	Potass. Iodide
Silver . . .	White	Black	Yellow
Lead . . .	White	Black	Bright yellow
Mercury (ous) . .	Black	Black	Olive
Mercury (ic) . .	White	Black	*Red
Bismuth . .	White	Black	*Dark brown
Copper . . .	Blue	Brown	Light brown
Cadmium . .	White	Yellow	—
Arsenic . . .	—	*Yellow	—
Tin . . .	White	*Yellow	—
Antimony . .	White	*Orange	—
Iron (ous) . .	Dirty white	Black	—
Iron (ic) . .	Brown	Black	—
Aluminium . .	White	White	—
Chromium . .	Green	Green	—
Zinc . . .	White	*White	—
Manganese (ous) .	White	Yellow	—
Manganese (ic). .	Brown	Brown	—
Nickel . . .	Green	Black	—
Cobalt . . .	Amethyst	Black	—
Barium . . .	White	—	—
Strontium . .	White	—	—
Calcium . .	White	—	—
Magnesium . .	White	—	—

* indicates that the precipitate is soluble in excess of the reagent.

CLASSICAL METHOD OF CHEMICAL MICROSCOPY

The principle is the production of crystals of a definite form, specific in the given conditions for a given metal. The crystalline form is identified by microscopic examination.

Aluminium.—This method relies upon the formation of the caesium-alum. The material is treated with sulphuric acid and then with caesium chloride. The mixture is heated and then cooled. The crystals formed are octahedra.

Antimony.—This metal is identified in the form of the pyro-antimonate of sodium. The crystals are of lenticular form.

Arsenic.—If arsenic is suspected, the material is tested with silver nitrate and ammonia is added. Crystals of arsenite of silver are produced. They are rhombic, needle-like in form and yellow in colour.

Barium.—The crystalline form of barium sulphate is rhombic. It produces small plates and in some circumstances clusters in the form of a cross.

Cadium.—The oxalate of cadmium produces rhombic crystals and prisms of some length. They frequently resemble those of lead chloride.

Calcium.—This metal is also examined in the form of the oxalate. The salt produces octahedra and star-like structures in the cold. Warm solutions produce cubes and prisms.

Cobalt.—This metal is detected in the form of the purpureo cobaltic chloride. Excess of ammonia is first added and then potassium permanganate in very slight excess. The solution is then boiled and cooled, and finally neutralized with a slight excess of hydrochloric acid. On cooling the solution deposits purple crystals of the purpureo chloride. They are octahedra. This test is inapplicable to small quantities of cobalt. It also requires experience and careful manipulation.

Tin.—The stannous oxalate shows a rhombic form and prisms. The crystals are often leaf-like in a cruciform shape or in that of an H.

Magnesium.—Magnesium ammonium phosphate if carefully prepared produces prisms of various types, and groups of cruciform shape.

A drop of the solution to be tested is placed upon a microscopic slide and a drop of ammonium chloride is added. A second drop of sodium phosphate is placed close to the first. The slide is then carefully heated over a water bath. A drop of ammonia is then used to unite the two drops. The drop is then rapidly cooled and allowed to stand until the crystalline precipitate has settled. Crystals of the rhombic type, plates, cruciform formations, stars, and other patterns are observed.

Potassium.—The chloro-platinate of potassium produces cubes and rhombic forms of a yellow colour.

Lead.—This metal is examined in the form of lead chloride. It produces plates and prisms. These sometimes show triangular shaped cavities at their extremities with the apex directed inwards.

Strontium.—Both the sulphate and the oxalate produce rhombic crystals which, however, often have the appearance of octahedra. On heating and recooling the rhombic form becomes apparent. The oxalate crystals often show a leaf-like appearance.

These methods are founded upon the classical procedure of crystallographic identification. Theoretically, they are sound, but in practice they suffer from certain disadvantages. In the first place, it is extremely difficult to achieve standardization of procedure with this type of operation on a micro-scale. Secondly, the crystalline formations described are not in all, or even in the majority of cases, specific. In the hands of highly experienced investigators, however, the metals and bases described can in most cases be identified. Considerable difficulties, of course, arise if more than one base are present.

These classical methods are not now regarded as of sufficiently refined a character. They have, in fact, little more than historical significance. Micro-chemical methods have greatly advanced in recent years. They will be discussed in principle and in particular as they apply to the examination of dusts.

THE APPLICATION OF MICRO-CHEMICAL METHODS TO THE EXAMINATION OF DUST

There are now three general methods of micro-chemical technique. They are distinct although related to each other. The oldest of the three is that of chemical microscopy. The second is micro-chemistry strictly so called, in which classical methods are adapted to small quantities by the use of miniature apparatus. The third is the method of the " spot " reaction, the most recent development of micro-chemistry. All these methods can be applied to the examination of dusts.

(a) Chemical Microscopy

Essentially the principle of chemical microscopy is simple. It is that many substances have a characteristic crystalline form by which they can be identified, but in practice identification by this method may and often does involve an elaborate technique. The apparatus required is, however, simple. It will be well to describe the minimum requirements for efficient work.

Microscopy.—An elaborate microscope is not necessary. It should have a substantial and heavy stand and the nose piece and stage should be designed to carry objectives and condensers of standard size. The body should have a draw tube with a soundly racking coarse adjustment and a fine adjustment of medium sensitivity. A mechanical stage is highly desirable, but not absolutely necessary. The microscope should be fitted with a polarizer and analyser. An Abbé condenser with iris diaphragm should be fitted. R. & J. Beck are among the manufacturers who produce suitable instruments. There are types of " crystallographic " microscope of a more elaborate design suitable for more precise work.

Binocular microscopes reduce eye strain and increase appreciation of depth and distance, but they are not essentially superior to monocular instruments.

It seems unnecessary to discuss microscopes in greater detail except to allude to the comparison and pocket microscopes.

The comparison microscope consists of two tubes with objectives whence the images are united by a system of reflecting prisms in a common eye-piece. Two specimens can thus be compared side by side. These microscopes are very valuable for the matching of colour.

The pocket microscope is useful for field work. Very small types of the size of a pencil are not of much use. Excellent instruments half an inch in diameter and about five inches long are made.

Apparatus.—Vessels are not normally used in chemical microscopy because almost all operations are carried out on the microscopic slide. At the same time some simple instruments are used. Glass rods drawn fine are of use for mixing and platinum wire mounted in a glass rod. A small platinum spatula with a spade-like end is helpful. Micro bunsen burners are necessary and platinum foil for ignition in place of a crucible.

Reagents.—It is essential that reagents should be contained in vessels so designed as to avoid contamination. The best form of container is a glass vial with a screw cap and plug which carries a glass tube drawn fine for the delivery of the reagent. With this arrangement the pipette never comes in contact with material other than the reagent. The reagents themselves must be frequently renewed for they become contaminated with sufficient traces of materials from the glass to affect their efficiency seriously.

Owing to the small size of the reagent vessels it is not advisable that they should stand on a reagent shelf. The reagents should be kept together in a wooden block pierced with holes to fit the vials. The whole should be fitted in a box.

When it was said that vessels are not generally used for chemical microscopy, it was not intended to exclude the application of certain operations which are not generally carried out on a microscopic slide. It may be necessary, as in other analytical work, to decant, filter, sublime distil or fuse. These operations, however, strictly belong not to the technique of chemical microscopy but to that of micro-chemistry. Those, however, which can be carried out on a microscopic slide will be considered. It may be remarked here that a small hand centrifuge is essential for certain kinds of chemico-microscopical work.

Other Equipment.—It is desirable, if not essential, that a special bench should be used for micro-chemical apparatus. It should be of reduced size commensurate with the miniature character of the apparatus. Convenient dimensions for the bench are a height of about 30 inches, a length of 4 feet and a breadth of 2 feet. The bench should be fitted with 6 or 8 drawers 3 or 4 on each side. It is also convenient to have a special cupboard attached in which the microscope and case can be kept. Neither reagents nor apparatus should be left on the bench when work is not in progress. The bench is designed so that the operator sits at his work.

It is not desirable that the top of the bench should be highly polished or covered with glass because with this type of work much reflected light is very trying to the eyes. A close grained wood painted black, unpolished but waxed is the most satisfactory. Where reagents are being used the work should be done on a piece of plate glass of convenient size. A large piece is clearly not necessary.

As a minimum the bench should be fitted with the following standing apparatus. Electric points and switches. Gas points. A microscope. Microscope slides and cover slips in suitable containers. A micro bunsen burner. Two glass dishes, one for clean and the other for waste water. Platinum wire, foil, and spatula. Fine drawn glass rods. Micro-test tubes in rack. Strips of filter paper in a suitable container. Capillary tubes. Two pairs of forceps straight and curved. Dissecting needles and micro-scalpels.

The bench should be well lighted preferably from the north and should be artificially lighted preferably with a fluorescent daylight lamp. If too close to the bench this form of lighting is a strain on the eyes.

Operations carried out on the Microscopic Slide.—In fact, most of the classical operations can be carried out on the microscopic slide with the aid of very simple apparatus adapted for this purpose. One of the essentials for this work is rigorous cleanliness of all glassware used. In particular the slides must be free from every trace of grease so that liquids will spread freely upon them. Capillary tubes should only be used once and then thrown away. Potassium bichromate and sulphuric acid is a good cleansing agent.

Solubility.—A small drop of water or other reagent is placed on the slide and spread with a thin glass rod. The material to be tested is placed close to the solvent and the slide is placed on the stage of the microscope or a lens is placed ready at hand if this is thought to be sufficient. With the glass rod the material is then moved into the area of the solvent and the effect observed immediately. It should be noted (1) If the substance seems to undergo simple solution. (2) If any intermediate product seems to be formed such as a hydrate. (3) If it is otherwise decomposed with the formation of some other substance. (4) If bubbles of gas are evolved. (5) If the material seems to remain unchanged.

It perhaps goes without saying that the next operation, that of heating the micro-drop, must be done with caution. The micro-flame should be turned as low as possible, and the slide held some distance above it. It should be moved from side to side while the process of heating goes on. Owing to the poor conductivity of glass, the spot is readily superheated. It must be cooled rapidly when the heating is discontinued or it will evaporate to dryness. Without special apparatus, it is difficult to observe the effects of heating the drop on the microscope stage. The effects can generally be watched with a good lens. In the case of soluble substances, it should be noted (1) If there is any colour change. (2) If bubbles not noted at normal temperature are formed. (3) If a precipitate is thrown down or the appearance of the drop suggests that the material is less soluble in the hot solvent than in the cold.

In the case of substances insoluble in the cold. (1) If the material dissolves wholly or partly. (2) If there is any change in colour either in the material itself or the solution. (3) Whether the physical form is changed without solution.

Evaporation.—This process is best carried out in a current of warm air. It can be supplied by a dentist's " blower," the nozzle of which is heated before the air is expelled through it. A spirit lamp, however, with a very small flame or a micro burner can be used. Whatever the source, very gentle heat is necessary.

Substances Insoluble in Water.—In the case of a substance insoluble in water, it may be important to ascertain in what common reagents it is soluble. This may help to identify the material directly. Alternatively, its solution will frequently be a necessary step in the examination. In microscopic solubility tests, as in all others, it is generally advisable to use reagents as concentrated as possible, so that the volume of the reacting constituents can be kept down. Concentrated mineral acids should first be tried and then acetic acid. If acids fail to dissolve the material, concentrated ammonium hydroxide should be used. It should be noted, of course, that these solubility tests apply to the detection of inorganic substances to which chemical microscopy is more generally applicable. The same technique should be observed as for aqueous solubility.

Decantation.—This is the most important of all preliminary operations of chemical microscopy because in a very large number of cases precipitates or insoluble matter have to be separated from supernatant liquor. It is, of course, not always practicable to avoid filtration to effect this, but resort should never be had to it if decantation will suffice. Decantation is of special value in connection with the examination of dust where it frequently becomes of importance to separate soluble material from extraneous insoluble matter which is often not amenable to chemical examination.

There are three methods of decantation (a) Mechanical. (b) By capillary and (c) Centrifugal.

(*a*) The mechanical method is discussed in detail by Chamot and Mason (*Handbook of Chemical Microscopy*, 1940, p. 10).

The slide must be scrupulously clean. A fine drawn glass rod is placed on the circumference of the drop containing the precipitate. It is drawn across the slide in the form of a narrow neck. If the operasion is carefully done the liquor only will follow the direction of the tip of the rod. When the neck is three or four millimetres long a rotatory movement of the rod will cause the neck to enlarge so that the drop has the form of two bulbs joined by a neck. A piece of filter paper folded double is then drawn edge-wise across the neck and the slide is immediately very gently warmed. The effect of these operations is to divide the drop into two, one containing the precipitate with a minimum quantity of liquor, the other, the supernatant liquor only. While this process is being carried out the slide must be inclined somewhat to facilitate the flow of the liquid.

If at the first attempt to form the neck with the rod, the precipitate tends to follow the direction of it, it is advisible to repeat the operation at a new point on the circumference.

(*b*) The capillary method is often the simplest and most effective method of decantation, but it is unsuitable in cases where the precipitate is light. The capillaries used should be about 8 cm. long and of an internal diameter of not more than 0·75 mm. The tip of the capillary is very carefully inserted into the drop in a vertical position. It is then inclined with great care through about 85 degrees and in such a way that the drop is not disturbed by anything approximating to a stirring movement. After removal of the liquor, the capillary is thrown away if the liquid is not to be examined.

(*c*) Since they cannot be carried out on a microscopic slide centrifugal methods are not strictly a part of chemico-microscopical technique. They will be discussed later (*infra* p. 30). It should, however, be noted that no method of separation is more appropriate for micro-operations in general. The use of a centrifuge may be an essential preliminary to chemico-microscopic examination.

Filtration.—Resort should not be had to filtration unless methods of decantation or centrifugal separation are impracticable, but there are many cases in which it cannot be avoided. One of the disadvantages of filtration in chemico-microscopy is that the precipitate is difficult to deal with in any filtration method applicable to liquids on a slide. If the filtrate only is required, the disadvantage is greatly reduced.

A simple method of filtration is to use a capillary about 1 mm. in diameter, the edge of which is accurately cut at right angles to the axis. This is essential if difficulties with the filter paper are to be avoided. The tip of the capillary is pressed upon a piece of *slightly* moistened filter paper cut to a diameter a little larger than that of the tube. Some workers prefer to cut a circle with the capillary itself. This, of course, corresponds to the internal dimension of the tube. The edge of the paper or tip of the capillary is then cautiously introduced into the drop. The filtered liquid rises in the capillary leaving the precipitate in part upon the paper and in part upon the slide.

The more elaborate methods of filtration depend upon the same principle but differ in the design of the capillary. A more satisfactory mounting for the filter paper is thick walled capillary tube with a bore of about a millimetre. Chamot and Mason (*loc. cit.*, p. 14) recommend a square piece of filter paper of the " extraction thimble " type. The paper is placed on the slide and the capillary tip applied to it firmly ; paper and tube are then moved until the paper comes into contact with the drop.

A rubber tube can be attached to this form of capillary so that suction can be applied if necessary. This may be required for larger drops. It is desirable that the tube should include a bulb to prevent the filtrate being sucked into the mouth.

There is also a syphon form of filtering pipette (*Edgeworth-Johnstone, J.S.C.I*, 50 182T. (1931)) the object of which is to deal with large drops without the aid of suction.

The disadvantage of this thick-walled apparatus is the difficulty of cleaning. This applies particularly to the Johnstone pipette, but also, although in a lesser degree, to the simpler forms. The advantage of the thin-walled capillary tube is that it is used once only. For all but special purposes, it is generally satisfactory.

Sublimation.—Substances can be sublimed from one microscopic slide upon another. The procedure is simple. The material to be sublimed is placed on the slide to be heated and the micro flame is applied not directly beneath the material but to the side of it so that the flame can be brought nearer to increase the temperature. A second slide is supported upon the first by means of two thin pieces of bakerlite or other substance of high melting point so that the upper slide is as close to the lower as possible. The two slides are held together in the fingers and carefully heated by bringing the substance to be sublimed closer to the source of heat. As soon as the sublimation begins the slides are withdrawn from the source of heat. Further sublimates can be made on the same slide by adjustment of the upper slide.

The Application of Reagents.—In all branches of micro-chemistry the method of applying the reagent greatly influences the result and nowhere more so than in chemico-microscopical operations. There are certain general rules which apply to all micro methods, and others applicable in particular to chemical microscopy.

First, reagents should be applied in as concentrated a form as possible in order that the volume may be kept down. Secondly, the volume of the reagent applied must be standardized in some way. This can be done either by the use of a platinum loop of standard size or by means of capillaries of uniform bore.

If the test is of the crystal-forming type as are most chemico-microscopical operations, the reagent is added at the edge of the solution to be tested and allowed to diffuse into it. The mixture is stirred in the case of other tests.

Gaseous reagents are applied either by exposing the slide with the test solution to a stream of the gas or the slide may (as in the case of ammonia) be held over the reagent bottle.

There are certain special methods of applying reagents. In some cases it may be advisable to apply the reagent after the cover slip has been placed over the test solution. If this is to be done it is advisable that the cover slip should be raised a little from the surface of the slide. A glass hair is a convenient support for this purpose. The reagent is, of course, applied at the point where the hair raises the cover slip.

Where very high concentration of the reagent is necessary, and where it must be present in excess at an early stage in the reaction, it may be advisable to apply the reagent solid. The size of the particle should be such that it does not exceed or only just exceeds the vertical dimension of the drop if it is to be present in large excess. If a lower concentration of the reagent is required, the size of the particle is suitably adjusted.

The converse of this process is the application of a liquid reagent to the material to be tested in a solid form. The test solution is spread out in a uniform layer on the slide. It is evaporated to dryness with gentle heat, and while the evaporation is in progress the drop is stirred so as to ensure a uniform film. The solution must not boil.

A drop of a saturated solution of the reagent is then placed 2 or 3 mm. from the dry film. With a glass rod the reagent is drawn across the film and allowed to remain in a channel bisecting it. The effect of this is for the solid under test to react with a minimum quantity of a saturated solution of the reagent.

Special Applications to Dust.—This outline gives an indication of the general technique to be applied to the making preparations for microscopical study. It is not practicable to discuss the identification of individual substances. For information on this subject the reader is referred to the chemico-microscopical literature and in particular to the classical work of Chamot and Mason, much of which is incorporated in Volume II of their *Handbook of Chemical Microscopy*. What is important here is to indicate the manner in which chemico-microscopical methods are applicable to the examination of dust.

The methods of chemical microscopy are more widely applicable to the identification of inorganic than organic substances. In fact the work of Chamot and Mason is confined almost exclusively to the examination of the former. This fact has considerable bearing upon the examination of dust by these methods since preliminary operations, appropriate to the material, have to be performed upon it. In criminalistic work it is rare to find dusts of simple composition. They are generally complex mixtures in which organic materials preponderate, such as textile debris from clothing, wax from the ears, solidified discharge from the membranes of the nose, gome from the fingernails, and fatty material from the hair. At the same time the investigation may be facilitated, and the method of attack determined, by the fact that certain suspected constituents are sought.

Whilst it frequently happens, of course, that macro quantities of the dust under examination are involved, it is generally more convenient to apply micro-methods to its examination. If, however, a macro quantity is available the preliminary preparation is facilitated.

A satisfactory general method is as follows :

If the test material is free from oils, fats or fatty acids, the dust should be extracted with a small quantity of water at first cold and afterwards warmed. According to the amount of material available a macro or micro-filtration is made. The result of the extraction and filtration is to separate water soluble inorganic materials from insoluble debris. If it is thought necessary the filtrate is concentrated and subjected to chemico-microscopic examination using the technique described.

If no further material is available the residue is divided into two parts. The first is ignited in a small platinum crucible or on a piece of absolutely flat platinum foil. The second part is retained in case an examination of the organic debris is necessary. The ash of the first portion will contain insoluble inorganic material not decomposed by ignition. Even if the initial quantity of dust is relatively large precautions should be taken with the ignited portion such that a very small quantity of ash can be adequately handled in the vessels used. It frequently happens that a bulky dust produces mere traces of ash. The ash is preserved and dealt with in the same way as the aqueous extract with such modifications as are necessary for examining insoluble substances.

Dusts associated with fatty material such as ear wax require different treatment. The fatty materials must first be separated. The wax is treated with a suitable solvent such as ether, petroleum ether or acetone. In the case of micro quantities (more common in this case) a capillary decantation is if possible made. This is generally practicable because of the low specific gravity of the solvent. If the quantity is very small this can be done on a microscopic slide with a depression. An ordinary slide cannot be used because of the rapid spread of the solvent. The fat-free residue is then taken up with water. If any insoluble matter is present, a second capillary decantation is made to separate the soluble and insoluble constituents. Since very little organic debris will be associated with the insoluble portion ignition is not necessary. The soluble and insoluble portions are then treated as before.

(b) Micro-Chemistry

Micro-chemical operations are those which utilize classical methods of analysis but carry them out in miniature apparatus capable of dealing both initially and finally with very small quantities of material.

The analysis of dust seldom calls for quantitative estimations. Micro-chemical methods applied to its examination are accordingly not of the most elaborate character. This does not alter the fact that it is often convenient to apply fundamental analytical operations on a micro scale.

Filtration.—Methods of filtration in micro-analysis are a reverse of those used in macro procedure. The micro-filter is, in fact, merely an elaboration of the capillary filter already described (page 24). An external source of suction, however, replaces the capillary effect. A very satisfactory form of micro-filter is described by King (*Analyst*, 1933, 58, 325). It consists of a thick-walled capillary tube drawn out at one end with the other ground flat at right angles to the axis. Round this fits a piece of thin-walled glass tubing, the upper extremity of which projects a little beyond the flat ground end of the capillary. This jacket is held in position by a piece of rubber tubing forming a collar. Filters are cut from stout filter paper with a cork borer. They must be of the same dimension as the capillary tube so that they fit inside the projecting walls of the jacket. The filter end of the tube is immersed in the liquid to be filtered. A tube is attached to the nozzle. This passes through a stopper into a vessel through which the air is sucked by means of a tube connection at its base. The vessel also contains a smaller one into which the filter tube passes to catch the filtrate. There exist, of course, other and more elaborate types of micro filter, but for the purposes of qualitative examination, the King filter is very satisfactory.

Ignition.—Ignition can, of course, be carried out in a micro-crucible, but the use of a micro-muffle ensures more efficient control over the material. That designed by Pregl consists of a straight piece of hard glass tubing round which is wrapped a piece of iron gauze heated by a burner. At the end remote from the burner another piece of hard glass tubing bent at right angles is fitted closely. A piece of iron gauze is also wrapped round the perpendicular limb of this tube. The material to be ignited is contained in a porcelain or platinum boat. Heating the perpendicular limb as well as the muffle tube ensures a steady draught and rapid ignition.

The advantage of the use of the micro-muffle is that it protects the igniting material from extraneous air currents, and enables the incineration to be carried out in a vessel smaller than can be used for crucible ignition.

Sublimation.– A simple apparatus for sublimation consists of a tube about 1½ inches long and ½ to ¾ inch in diameter. A small glass thimble is fused into the bottom. The top carries a cork and an outlet tube. The material to be sublimed is put into the thimble and a small microscopic slide rests over it. The thimble is heated in a suitable bath or with a micro flame and the sublimate is deposited on the slide. The advantage of the use of a tube of this type is that the sublimation can be carried out under reduced pressure.

Distillation.—There are circumstances in which the distillation of dust extracts will give indications concerning composition not readily obtainable in any other way. Micro-distillation apparatuses after the model of Behrens are very simple and elegant. They consist of a glass bulb drawn out fine on its left side and bent at right angles to the bulb with a second outlet tube on the right larger and bent at right angles downwards. This part of the tube enlarges towards its extremity. There is an elbow blown with a bulb-like joint, the final section of this enlarged tube being bent at this elbow again at right angles in the vertical direction.

To charge the still a rubber bulb is attached to the righthand end, the narrow tube on the left is inserted in the liquid and the rubber squeezed. Thus the liquid enters the first bulb. The narrow tube is then filed short and sealed off. The bulb at the elbow is inserted in ice and the first bulb heated with a micro flame or in a suitable bath. The distillate collects in the bulb at the elbow.

Decantation.—The simplest and most efficient method of decantation is to centrifuge the deposit down. This method makes possible not only efficient separation but proper washing of the precipitate or other insoluble matter.

Capillary tubes 1–1·25 mm. in diameter should be used. They should be about 8 cm. long. These tubes are readily adapted for whirling in the small centrifuge by fitting the cups with corks which are bored with holes to fit the capillary firmly. The cork should not be too deep and the capillary must be inserted with care.

The capillary is fitted with the liquid to be centrifuged in the usual way, sealed off at the free end and the liquid shaken down. It is then inserted in the centrifuge cork with a second tube filled with water in the counterpoising cup and whirled.

If the deposit is to be washed, the supernatant liquor is withdrawn with a capillary inferior in diameter (about 0·5 mm.) to the centrifuge capillary. Water or other washing agent can be introduced with a similar capillary and the centrifuging repeated.

As in all other micro-chemical operations, that of transference from the capillary, if it is necessary, is the most difficult. If the deposit is relatively large the extreme tip of the capillary can be broken off and the deposit blown or washed out with a trace of water into a suitable vessel. This method is unsafe if the deposit is small. In this case the best method is to introduce a trace of water into the tube containing the deposit with the narrower capillary, and to mix and withdraw it with the same.

There is no other method of decantation as satisfactory as this. In some cases it is, of course, possible to use the capillary method of decantation. Whilst applicable in some cases it is generally less efficient, particularly if the deposit is to be washed, and often a longer process.

Special Applications to Dust.—Other than the considerations dealt with under chemical microscopy there are no special aspects in connection with the application of these methods to dust. In general the material, after the preliminary treatment indicated, can be dealt with in the same way as any other sample for micro-analysis.

(c) The Spot Reaction

The technique of the " spot " reaction in micro-chemical analysis has been increasingly utilized in recent years. The method is greatly recommended on account of its simplicity. This is, in general, one of its dangers. In terms of manipulation the technique is certainly simple, but the tests are subject to many limitations, and they are often influenced by variable factors not easy to control. These considerations have a special importance in connection with qualitative examination, because quantitative work can generally be independently checked. This is often not possible when minute traces not amenable to alternative forms of test are to be identified.

If its limitations are recognized, however, this technique is of great value. Qualitative tests can be carried out with other apparatus, but the essential feature of spot testing is that the operations can be performed on filter paper. Filter paper is the favourite medium first because the colour reactions upon which most of these tests depend are readily studied in this way, and secondly because the capillary effects associated with this medium can be utilized in certain types of reaction.

There are three primary factors associated with spot tests which are the foundations of its mechanism. These are (1) The limit of identification. (2) The limit of concentration and (3) The limit of proportion.

The limit of identification means the smallest amount of material recognizable in terms of the reaction. This is generally expressed in terms of gamma or 10^{-3} mgm.

The limit of concentration means, the smallest concentration of the solute to which the test is sensitive.

The limit of proportion means the smallest proportion of the substance sought which can be identified in the presence of one or more other constituents.

The third factor is one of very great importance because although many of the tests are specific, the presence of other substances may substantially reduce their sensitivity or inhibit the reaction altogether.

It is not necessary to discuss the preliminary treatment of the material since the technique already described in connection with the first two methods of micro-analysis also applies for the spot reaction, but there are certain special considerations which must be observed.

Since the utility of the spot test depends upon the limit of concentration, and since in the particular case it cannot be known if this has been exceeded, it is essential that the material examined should be in as highly concentrated a solution as possible. This, of course, applies to all micro-determinations, but in a very special sense to the spot reaction. Too great a dilution of the test solution is a prime cause of failure in the application of the test. There are two means by which maximum concentration can be effected. The first is that all test solutions should be concentrated to the greatest limit, and the volumes at all stages of the operation should be kept as low as possible. Although in the case of dusts the tests carried out are nearly always qualitative, every means must be adopted to avoid loss in the preliminary stages. The second method is concerned with the application of reagents.

The Application of Reagents.—In macro as in micro-chemical operations reagents are normally added to test solutions. In carrying out tests on filter paper this procedure is often reversed, that is to say that the test is carried out upon paper which has been impregnated with the reagent and dried. The advantage of this method is that the degree of concentration of the substance sought in the reacting system is not altered by the addition of a liquid reagent. Wherever practicable, it is advisable to introduce the reagent in this way.

In impregnating paper, however, it is necessary to ensure that the reagent is uniformly distributed. This is best done by applying it with an artist's atomizer. The instrument consists of two capillaries with pipette nozzles set at right angles to each other. The vertical tube is immersed in the solution while the operator blows through the horizontal tube. A very fine spray of liquid is thus expelled.

When tests are made under other conditions the reagent is generally added to the test solution. It should be in as concentrated a form as possible for the reasons already stated. The mixture should be stirred with a very fine glass rod or centrifuged if the test is carried out in a capillary.

Separation of Radicles.—Whilst a number of reagents used in spot reactions are specific for a given radicle, this is not always the case, and if radicles which interfere with the required reaction are present they must be separated. It is not necessary to discuss here the classical methods of separation on a micro-scale. They depend essentially upon the application of technique already described. There exist, however, certain methods of separation which can be carried out on the filter paper itself. These are of two types. (1) The capillary effects associated with the paper itself may be utilized since products of the reaction of different solubilities show different diffusion rates. The result of this is the formation of independent zones of colour corresponding to different radicles. (2) Interfering radicles may be precipitated by the prior addition of a reagent which throws them down.

An example of (1) is the detection of bismuth with an aqueous solution of cinchonine acidified with nitric acid and containing potassium iodide. In the presence of bismuth alone an orange-red spot is produced. Coppet, lead and mercury interfere if the test is carried out *in vitro* in the ordinary way, but if the test is made upon filter paper the capillary separation it effects produces four independent zones (1) a white centre due to mercury, (2) an orange ring due to bismuth, (3) a yellow ring due to lead, (4) a brown ring due to copper.

As an example of (2) alizarin forms a lake with a number of metallic hydroxides, and that produced by aluminium is a delicate test for the metal. The reaction, however, is evidently not specific since iron, chromium, uranium, thorium, titanium and manganese also form lakes with alizarin. These metals can, however, be suppressed by carrying out the reaction on paper impregnated with potassium ferrocyanide. This precipitates the interfering metals whose ferrocyanides are insoluble. The soluble aluminium ferrocyanide alone reacts.

Another example of the same method is the detection of silver by means of the p. dimethylamino-benzal-rhodanine, the most sensitive test at present known for silver. Mercurous and cuprous ions and the cupric ion in neutral solution interfere with the reaction. In the presence of hydrochloric acid, however, the reactions for copper and mercury are suppressed.

A specific and particularly interesting example of separation is the identification of ferrous iron by means of $\alpha\alpha'$-dipyridyl. This is a very sensitive test for ferrous iron of the order of 0·2 gamma. Ferric iron gives no reaction with the reagent. This test has importance in connection with the analysis of iron gall ink (*infra* p. 94). It is obvious that where ferrous iron is to be identified in dust, any preliminary treatment must exclude the possibility of the oxidation of the iron, so that an aqueous or non-oxidizing acidic extract without preliminary ignition must be used for the test.

Special Applications to Dust.—In the strictly technical sense, there are no special applications to dust. But since the spot reactions require very simple apparatus they are often of considerable value for field work. As Emich and others have suggested, the future will produce a specific spot reaction for most if not all radicles. But this is not the case at the present time. It seems important to emphasize this so as to ensure that the limitations of the technique are kept in mind. If, however, account is taken of these limitations, the method is of great value for the examination of dusts and other micro-chemical operations.

Choice of Micro-chemical Method.—It is not possible to devise rules for the choice of method in the micro-chemical examination of dust. In the first place not only the circumstances influence the decision but the individual taste of the analyst. Those highly practised in chemico-microscopical technique or in the applications of the spot reaction may decide to use one of these methods independently of the circumstances. For it must be borne in mind that even when macro-quantities of material are available a micro-chemical technique may still be applied. In general the best rule to follow is that of using the method in which the operator is most skilled and experienced.

On the other hand it is obvious that the three methods described are related to each other, because in most cases the preliminary operations require the application of a strict micro-chemical operation of some kind, that is to say one involving the use of miniature apparatus. Every operator must therefore be conversant with these methods.

Since, however, the examination of dust is generally of a qualitative character, methods of chemico-microscopy or of the spot reaction are usually the most convenient. The strictly micro-chemical methods are often more suitable for quantitative work. They involve the use of the quartz micro-balance and micro-volumetric apparatus.

INTERPRETATION OF RESULTS

The interpretation of the results of an inorganic analysis of dust requires considerable experience. It calls also for discretion. All analysts are familiar with the method of interpretation commonly called " the most probable composition." It is applicable only when a complete analysis of all bases and acid radicles has been made quantitatively, and therefore cannot generally be applied in the case of dust.

This does not prevent valid interpretations being made within limits which must be clearly recognized. If, for example, carbonates and chlorides are found associated with calcium and sodium it is clear that the dust contains either sodium chloride and calcium carbonate or calcium chloride and sodium carbonate. The physical appearance of the dust when examined microscopically may sometimes assist in the interpretation. Crystals of a certain form may be recognized or the deliquescent or efflorescent nature of substances present in the dust may be observed. Again, if copper were found associated with potassium, sulphates and chlorides the microscope might reveal which acid radicles and which bases were associated. Even in the many cases where this is not practicable, if the acid radicles and bases present are known, the results can be provisionally interpreted in such a way as to produce useful results. Inferences which go beyond the facts, however, must be avoided.

In certain cases positive inferences can be drawn. These generally belong to that exceptional category in which quantitative results are available and can be interpreted. Thus Locard (*Manuel de Technique Policière*, 87) quotes a case of a quantity of occupational dust found in the clothing of suspected coiners. The dust was abundant and proved to be of a metallic type. An analysis by classical methods was practicable. The dust was found to consist of lead, antimony and tin in certain proportions. Those proportions were later found to agree substantially with the composition of an alloy of which certain counterfeit coins were found to be composed. The inference was that the suspects had manufactured the coins in question. This conclusion was ultimately confirmed.

To return to a typical illustration, however, if traces of these metals were identified without quantitative estimation, this would be presumptive evidence that it was a counterfeiter's occupational dust, although the inference would be less positive than in the former case.

These illustrations are examples of the attitude which should be adopted to facts of this type. We are not here concerned with definitions of the nature of scientific and judicial proof. It is merely necessary to indicate that the interpretations of laboratory results in criminalistic practice are not useless because they lack the precision which the ideal type of investigation achieves.

THE APPLICATION OF MICRO-CHEMICAL METHODS TO THE DETECTION OF ORGANIC SUBSTANCES IN DUST

As in the case of micro-chemical operations already considered, the value of the results will, to a large extent, depend upon the proper conduct of the preliminary operations. In general, the detection of organic materials in dust calls for more latitude and discretion in the methods of preliminary attack.

The method of direct inspection, and in certain cases physical separation of organic constituents is more important than in the case of examination for inorganic materials. This is because an ultimate inorganic analysis in which, for example, a basic and acid radicle are identified can be more readily interpreted than an ultimate organic analysis of complex mixtures of this character. If it is possible to detect under low magnification and, after inspection, mechanically to isolate matter of characteristic appearance, this should be done. And it should, of course, be borne in mind that by this method material may be isolated which is not amenable to chemical examination, but which requires the application of other means of identification.

This form of examination is, however, not sufficient. It is necessary to apply a general form of preliminary treatment on a micro-scale the object of which is to separate broad classes of organic substances from each other. There are two methods of preliminary treatment of value in this connection (1) Distillation and (2) Extraction. This is, in effect, to apply on a micro-scale the principle of classification applied by Lucas (*Forensic Chemistry*, p. 286) to toxic agents, namely, the prior separation of volatile substances isolated by distillation and non-volatile substances extracted by solvents. This method also has the advantage that an examination of the same sample for inorganic non-volatile materials may be made when the residues remaining from these operations. This is an advantage where limitation of material makes it necessary or at least desirable.

Distillation.—It is practicable to use Behren's micro-still (*supra.* p. 29) for this purpose. For this type of examination it is desirable that the distillation should be with steam. Micro-steam distillation apparatuses are not, in our experience, easy or satisfactory to manipulate, but mechanically it is not difficult to adapt the Behren's still for steam by means of the attachment of a small " boiler " with a fine capillary outlet which is attached to the tube of the distilling bulb and so arranged that the nozzle passes beneath the liquid to be distilled. In practice it is generally sufficient, however, to distil by direct heat. Apart from this modification in technique there is another which has special applications to the examination of dust.

The material to be distilled is seldom completely soluble in water, but it may not be sufficient to distil the aqueous extract alone if it is thought that substances mechanically or otherwise associated with the solid matter but insoluble in water might be separated from the menstruum by distillation.

In this case the dust itself must be introduced into the distilling bulb. This process requires very careful manipulation. It can best be done, if the quantity is relatively large, by means of a capillary with a wide end with the narrow outlet cut off short but inferior in diameter to the filling tube of the still. To introduce the material, the filling tube is filed off short close to the bulb. The narrow end of the capillary into the wide end of which the material has already been introduced is passed into the filling tube and the material pushed into the bulb with a platinum wire. The water is then introduced not by suction from the other end of the still as in the case of a solution but by means of a capillary pipette with a bulb through the same orifice of the still. A drop of the water may be passed through the funnel-like capillary to wash down any adhering particles.

If the quantity is small, it is better to make a suspension in water. This is taken up with a capillary and introduced as before into the distilling bulb. With small quantities of solid matter even light material can generally be dealt with in this way.

Extraction.—For the purposes of qualitative examination it is possible to adapt the Stas-Otto principle of successive extraction on a micro scale.

The material is first extracted with warm alcohol. For small quantities this is best done by centrifugal decantation in the manner already described. It is, however, advisable to use a capillary of somewhat larger diameter of the order of two mm. The process is one of preliminary digestion so that it is advisable to introduce a fine stirring rod. This cannot conveniently be done with capillaries of smaller diameter. For larger quantities capillaries of increasing size can be used. The material is digested with stirring and separated by centrifuging. The insoluble portion is retained, and extracted with ether.

Evaporation of the alcoholic extract can be spontaneous or assisted by a current of slightly warmed air.

Owing to the high incidence of solubility of organic compounds in alcohol most substances likely to be amenable to examination will be isolated by this extraction.

The alcoholic dry extract is treated with acidulated water in the same way as with alcohol and the insoluble matter is separated and retained. This extract is then treated with ether, petroleum ether or chloroform and the ethereal layer separated. The acidulated extract is then made alkaline and extracted with chloroform.

This scheme of separation yields six extracts and residues (1) Insoluble in alcohol, cellulose, starch, textile fibres, fats and oils, debris from dust. (2) Ethereal extract from insoluble matter, mainly fats or oils. (3) Insoluble from acidulated water. (4) Ethereal extract from acidulated water, certain synthetic drugs. (5) Chloroform extract of alkaline water, soluble alkaloids. (6) Insoluble from alkaline extract, insoluble alkaloids.

(7) The distillate by steam or direct distillation will contain volatile material such as volatile acids, phenols and volatile oils.

This method of separating the constituents of dust has the advantage of being systematic, and will isolate certain classes of organic compounds if they are present in the dust. A scheme of separation is necessary because the mere examination either chemically or optically of dust to which no preliminary method of separation has been applied does not generally yield results of much value. But a procedure of this kind cannot, of course, be followed slavishly. From a criminalistic point of view the term " dust " is not precise since samples may vary very widely both physically and chemically. Physical methods of separation may in some circumstances be the most suitable, or a microscopic examination of greater use than any chemical test. But where these methods are not applicable those of successive extractions can and do make the constituents of the dust available in a form which may facilitate identification of some of the constituents.

Examples in Practice.—Organic materials which are constituents of dust can obviously be of a very varied character. A discussion of their identification in detail would clearly be impossible. What can be done, however, is to indicate by means of illustrations from practice how the preliminary technique of examination can be brought to bear upon the problem.

Inter alia such substances as organic compounds, starch, dried blood, perfume, hair, sugars, dyes and shellac may be found in dust associated with clothing. Below are some examples of the manner whereby these materials may be identified.

Starch.—A relatively large quantity (about 20 mgm.) of the dust was available. About 5 mgm. were distilled but the distillate yielded nothing of importance. A second portion of 5 mgm. was treated by extraction. Some white particles were observed in the insoluble matter from the alcohol extract. It should be noted that these had not been noticed in the original dust probably because they were associated with material soluble in alcohol which had originally hidden them.

The material was consistent with the appearance of starch. The distillation residue was accordingly tested with iodine. It gave a strong blue reaction. A microscopic preparation was made of a portion of the alcohol extracted sample. Wheat starch was identified.

Fatty Substances and Hairs.—After an ether extraction of a small sample of alcohol extracted dust (10 mgm.) fatty material was identified and some small fragments of hair afterwards identified as human. These were not observed in the original dust.

Organic Compounds.—In this example some 30 mgms. of the dust were fortunately available. First, the distillate from the acidified aqueous suspension of dust gave a reaction for cyanides with ferrous sulphate and ferric chloride. The portion reserved for extraction was carried to the final stage for the separation of alkaloids. Strychnine was detected in the alkaloidal extract. This was independently confirmed as a pharmaceutical or chemical dust of considerable evidential value.

Dyes.—Most dyes can be detected in the first alcoholic extract. In three examples, two of clothing and one of ear wax containing dust, methylene blue and methyl violet were first detected in this way. It should be noted that in dealing with ear wax, the alcoholic extract is made first so as to prevent, as far as possible, the association of fatty material with other compounds soluble in ether as well as alcohol.

Shellac.—In this example some 5 mgm. of the dust were available. Examination with the lens revealed the presence of particles of a resinous character and of yellow-brown colour. In alcoholic extract a large proportion of the material went into solution. The dry extract also had a resinous appearance. Solubility tests showed that the extract was insoluble in ether and completely or to a large extent in benzene. It was a reasonable inference that the substance was shellac.

These are representative examples of the manner whereby the general technique described can be utilized for the isolation and identification of organic material in dust. It is, of course, obvious that the results of an analysis of this kind must often be negative but positive results are found in a sufficiently high proportion of cases to justify a systematic examination.

PRELIMINARY EXAMINATION OF ORGANIC DUST

If the quantity of materials available justifies it, the preliminary examination already described may be carried out. The aqueous and alcoholic extracts of the dust should be carefully examined for colour and for finely divided particles which may remain in suspension. The insoluble matter both in water and alcohol should also be examined. It is also desirable to make an ether extract of the dust for the purpose of recovering fatty substances which may be contained in it.

As large a portion of the dust as is practicable should be gently ignited and the smell carefully noted. The manner in which the material ignites should also be observed. It is important to note, for instance, if the dust burns quickly, or if it chars and swells.

The behaviour on heating may give a clue to the presence of one of the simpler organic acids. Formic and acetic acids are recognized by their smell. Oxalic acid evolves gas but does not char, succinic acid does not char, whilst tartaric and citric acids char rapidly and slowly respectively. Owing to the mixed nature of most dusts it is not ordinarily possible to observe these reactions but they illustrate the necessity for close observation of the results of these preliminary tests.

PARTICULAR CASES

There are certain special cases which are important from a forensic chemical point of view. Where the dust is abundant a careful examination of it should be made with a lens with a view to the separation of certain constituents which may be identifiable by direct inspection. In some cases these can be mechanically separated from other constituents. In other cases the coarse screen effects this separation to a great extent since it is only the large particles which can be recognized and separated.

Tobacco.—This is a constituent of a type which can often be recognized and separated. A determination of the class of tobacco may often be of great evidential value. Although tobacco is mainly of organic

IDENTIFICATION OF ALKALOIDS (Locard)

Alkaloid	Sulphuric Acid	Fröhde's Reagent	Mandelin's Reagent	Ammonium Tellurate	Nitric Acid	Potassium Ferrocyanide
Aconitine	Yellow-brown then violet	—	—	—	Yellow-green (cold)	—
Atropine	Brown (warm)	Brown-green then brown	—	—	—	—
Berberine	Olive-green	Red then yellow	Yellowish red	—	—	—
Brucine	—	—	—	—	Bright red	—
Caffeine	—	—	—	—	—	Orange
Cinchonine	—	—	—	Green	—	—
Chelidonine	Pale green then brown and red	—	—	—	—	—
Cocaine	—	Dirty green then blue	Blue-green	—	—	—
Codeine	Dark brown-green	Yellow-green then red-violet	Olive-green then brown	—	—	—
Colchicine	Yellow	Cherry-red	—	—	Violet then brown	—
Curarine	Red then red-violet	—	—	—	Purple	—
Emetine	Greenish-brown	Red then green	Brown	—	—	—
Morphine	Red then violet	Violet, green, brown, yellow, blue-violet	Reddish —	—	Orange	White becoming blue
Narceine	Yellow then red	Green (cold) Red (warm)	Violet then red-orange	Yellow then dirty green, violet	Yellow	—
Narcotine	Yellow then red (warm)	Green then yellow and red	Red	Rose	—	White
Nicotine	—	Yellow then red	—	—	Yellow	—
Papaverine	Blue-violet	Red-violet then blue yellow and decolourized	Bluish-green	—	—	—
Piperine	Yellow then brown, green-brown	Yellow, brown and black	Dark blood red	—	—	—
Quinine	—	Green	—	—	—	Green
Strychnine	—	—	Violet then rose on dilution	—	Light yellow	Bluish
Thebaine	Red then orange	—	Red-orange	—	Yellow	—
Veratrine (Cevadine)	Yellow then orange and red	—	Yellow then orange and red, violet	—	Yellow	—
Yohimbine (Quebrachine)	—	—	Violet	—	—	—

origin an examination of the inorganic constituents may serve to identify it.

Thorpe quotes the following figures for certain classes of tobacco.

TOBACCO ASH

Thorpe's Dictionary of Applied Chemistry.

Kind of tobacco (*a*)	Total Ash	Potassium Chloride	Lime	Magnesia	Potash	Sand
	%	% (*b*)	% (*b*)	% (*b*)	% (*b*)	% (*b*)
China . .	14·8	3·7	31·1	12·7	14·4	2·1
German . .	25·9	25·0	35·7	6·5	—	0·9
Havana . .	21·4	12·7	33·1	5·3	11·8	1·8
Java . .	18·8	19·6	22·3	8·5	14·1	1·7
Kentucky . .	18·0	2·4	29·5	6·8	16·8	5·3
Latakia . .	18·2	4·1	34·7	5·5	19·6	0·9
Manila . .	21·4	6·5	33·3	7·2	16·3	0·6
Turkey . .	12·9	19·3	22·5	9·2	14·5	1·8
Virgina (ripe) .	15·0	2·5	18·9	6·7	34·2	1·0
Virginia (bright)	12·3	7·0	21·7	12·4	22·2	1·3

(*a*) The tobacco was dried at 100 degrees C. before being analysed.
(*b*) Calculated on the ash.

A quantitative analysis is necessary if definite conclusions are to be drawn. Even when the material is abundant micro methods of analysis must be employed. Many of the methods previously described (*page* 25 *et seq.*) can be applied quantitatively.

Textile Fabrics.—In dust from clothing, fibres due to the cloth itself are always found, but a careful search should be made for foreign fibres. Their colour should be noted and if white they can be tested with such reagents as iodized zinc chloride, iodine in sulphuric acid, and cuprammonium sulphate. Certain textile fibres can be identified in this way. The tests, however, require experience in interpretation, particularly if small fibres are under examination.

If the fibres are coloured the nature of the dye can also be determined. In this connection, however, it must be borne in mind that the actual isolation of a fibre of a definite colour is often of greater value as evidence in itself than is a determination of the nature of the dye staining it. A portion of such fibres must always be preserved untouched, so that they can be compared with others found upon the scene of the crime, associated with the clothing of a victim, or in other circumstances.

These are examples of materials of large particle size which in our experience can be dealt with in this way.

Gome.—The fingernails should not be neglected as a source of occupational dust. It is always to be found in the form of what is known as gome, that is to say a mixture of dusts with fatty materials. As much as possible should be removed and the material examined for general appearance and colour.

Blood.—In the case of butchers and slaughterers the gome is generally dark red or brown, and the consistency will be remarkably greasy. It should be tested for blood using Adler's method as modified by Medinger (*Rev. Inter. de Crim.*, 1931, 7, 493, *also Rhodes*, *Manufacturing Chemist*, 1937, *VIII*, 9, 287). This is among the most sensitive of all tests known for blood. The colourless leuco-base of malachite green dissolved in dilute acetic acid produces a green and then a dark blue-green colouration with blood. The test does not, of course, distinguish between human and animal blood.

Metals.—Those who carry quantities of gome in their fingernails are generally mechanical workers of some kind. Traces of metallic dust are not infrequently found in deposits of this type. The gome must be treated with ether to remove the fatty substances. It is then often possible to identify metallic fragments by inspection. Where this is not the case the metal is dissolved in acid and its nature determined. It is of interest to note here that in a case of coining investigated at the laboratories of technical police at Lyon, metallic dust was discernible with the naked eye in certain parts of the clothing of the suspected man. These metals were identified, namely, as lead, antimony and tin.

SUMMARY

It is seldom possible to make a complete examination of dust and determine its precise nature by chemical or any other means. What the forensic chemist must aim to do is to make a general systematic study of the sample and then investigate its outstanding characteristics in detail. It is not possible to devise methods of particular treatment in advance, for each case has to be considered on its merits.

It is important to bear in mind that there are other methods of investigation besides chemical methods which throw light on the composition of dust. These are beyond the scope of this book, but a word must be said concerning the responsibility of the individual who first examines the sample. In many cases the chemist undertakes this important preliminary operation. He must therefore acquaint himself with the general nature of dusts and be able to recognize the evidential importance of constituents which he may not be able to examine himself. Dusts may and often do contain vegetable debris, seeds, spores, parasites, and bacteria to which chemical methods cannot be applied. Human secretions may be mixed with it which are not amenable to examination by chemical methods. There are many other substances also whose examination requires the co-operation of the physician, the botanist, and the bacteriologist. It is the responsibility of the preliminary examiner to decide the types of investigation which are necessary, their relative importance, and thus in what order they should be carried out. It is for this reason that so much depends upon the preliminary examination.

THE EXAMINATION OF BLOOD GROUPS

An increasingly important aspect of the indirect identification of the person is the determination of blood groups. It is questionable how far the technique of examination can be appropriately called a chemical problem. Without special training and experience the chemist should not undertake the examination, but some description of blood groups and their identification seems to be appropriate here.

The fact that human blood is known to fall into four groups which can be identified is of great forensic importance from the point of indirect identification. Whilst it is clearly not possible to distinguish individuals in this way groups can be distinguished from other groups. In a negative sense the evidence supplied may be definite. If, for example, a blood stain found upon a weapon is of a different group from the blood of the alleged victim of the weapon, the crime could not have been committed with that weapon. On the other hand, evidence of a positive kind exists if a blood group of a more uncommon type is found upon a weapon or elsewhere since it may presumptively connect it with a particular person.

A further use of the group test is the example in which a suspected person declares that a blood stain upon his clothing originated from his own blood from a cut finger or bleeding nose. If the blood group differs, identification is clearly disproved, whilst agreement may indicate but does not, of course, establish identity.

Classification and Nature of Groups.—There still exist differences in nomenclature but the international classification of Landsteiner is now generally accepted, namely the groups O, A, B and AB. The characteristics of these groups are determined by the presence in the blood and serum of substances which have been described as agglutinogens and agglutinins. The agglutinogens exist in the red corpuscles, whilst the agglutinins are found in the serum. Agglutinogens are designated A and B, and the agglutinins a and b. This explains the classification. Group A contains agglutinogen A only; B contains B only; whilst AB contains both. In group O, both are absent. In regard to the agglutinins, b is associated with A; a with B; O with ab; whilst AB is not associated with an agglutinin.

Principles of the Test.– The principle of the test is that bloods of corresponding groups cannot agglutinate with each other. Landsteiner's definition states that: " In a given blood containing a given agglutinogen, the serum will also contain agglutinins which are incapable of acting upon the said agglutinogen and thus bring about agglutination." On the other hand, unlike agglutinogens and agglutinins bring about agglutination if the bloods containing them are mixed. It is thus possible with a pair of serums and one confirmatory test to determine into which group the blood falls. For example, A and B will both agglutinate AB, B will agglutinate A and A,B. Thus if both results are positive the group is AB. If A is negative and B is positive, the group is A; and if A is positive and B is negative the group is B. O, on the other hand, is negative to all other groups. The negative result can be confirmed by treating the serum of the unknown blood with the corpuscles of Group A and B. Since the serum of Group O is unique in containing both agglutinins a and b, the reaction is positive in both cases.

Method of Determination.—The serum of the blood to be tested may be mixed with the corpuscles of known groups or sera of known groups may be used to test the blood under examination. The second procedure is generally more convenient.

Two drops of the sera of Groups A and B are placed on a microscopic slide. A small drop of the blood to be tested is then intimately mixed with the two drops. A fresh rod should be used for each test. If the test is being made upon an individual, the blood should be freshly drawn and transferred to the serum before coagulation.

The clumping of the corpuscles can be seen with the naked eye but it is preferable to examine the mixture with a lens.

In order to increase the reactivity of the blood, Martley (*Analyst*, 53, 1928, 15) recommends the removal of the serum by treatment with physiological saline.

In dealing with stains the same author (*Trans. Med. Leg. Soc.*, 18, 1923–24, 77–9) places the stained material in a small test tube with distilled water and incubates it, after sealing, for twenty-four hours. A clear solution is obtained from this extract by suction into a small pipette packed at the nozzle with fibres of filter paper. The solution contains the serum and must thus be tested with blood corpuscles.

The following tables make the reactions clear :

Using Serum of	*Corpuscles*			
	Group AB	Group A	Group B	Group O
Group AB	—	—	—	—
Group A	+	—	+	—
Group B	+	+	—	—
Group O	+	+	+	—

Using Corpuscles of	*Serum*			
	Group AB	Group A	Group B	Group O
Group AB	—	+	+	+
Group A	—	—	+	+
Group B	—	+	—	+
Group O	—	—	—	—

+ = Positive reaction
— = Negative reaction

In the hands of an experienced manipulator the test is extremely sensitive and can give positive results using very small quantities of blood. It must be borne in mind, as we have stated, that serious errors can arise if the technique of the test is not fully understood. Those performing the test must be fully experienced in biological and bio-chemical tests.

Developments of the Group Test.—The classic work of Landsteiner and his collaborators has established that blood can be further differentiated into sub-groups. Thus they have identified Group A as being divisible into A_1 and A_2. (*See also Harvey*, *Indian Journ. of Med. Research*, 17. 1936, 1307–11.) Substances described as P and Q, M, and N have been identified. Locard indeed considers (*Traité de Crim.*, *IV*, 558) that eighteen groups can now be identified, namely OM, ON, O MN, A_1M, A_1N, A_1MN, A_1A_2 M, A_1A_2 N, A_1A_2 MN, BM, BN, B MN, A_1B M, A_1B N, A_1B MN, A_1A_2 BM, A_1A_2 BN, A_1A_2 B MN.

Locard, however, points out that whilst under carefully regulated experimental conditions reliable results may be obtainable, that in practice the classic four groups can alone be verified in ordinary laboratory work.

From a theoretical point of view, however, the investigation is of great importance. Whilst it seems improbable that tests will be devised which will make possible the individual identification of blood, the multiplication of identifiable groups makes a closer approximation to personal identification possible.

SEMINAL STAINS

The semen of the individual is of the same agglutinative group as the blood of the same individual. The tests described suitably modified can also be applied to the examination of seminal stains. Dervieux (*Le Diagnostic des Taches en Medecine Légale*, *Paris*, 1912) and others have described tests using a serum prepared from rabbits which have been injected with human sperm. This serum reacts with blood and with sperm. Dervieux has stated that the sperm taken from the individual from which the serum was prepared reacts more strongly with the serum than the sperm of other individuals. This interesting observation has not been confirmed. Tests of this kind are very difficult to interpret, and it is doubtful if they could be applied in ordinary practice to the diagnosis of individual seminal stains.

PART TWO

APPLICATION OF CHEMICAL METHODS TO THE PROOF OF *CORPUS DELICTI*

CHAPTER III

STAINS

It is not necessary to discuss the definition of the term *corpus delicti* in detail. The term, which cannot literally be translated, means the " corpus " (content) of the act. It is often wrongly interpreted as the body of the victim. This misconception arises from the fact that in certain special circumstances the body of a victim may be *corpus delicti* as, for example, when the discovery of the body depends upon proof of the commission of the crime. In general, however, the term means the existence and therefore demonstration of a fact or facts which establish that a crime has been committed.

It can thus be assumed in general that any material clue which is to be interpreted not for the purpose of identifying the person but primarily for the purpose of determining the nature of the crime or the manner of its commission can be classed as *corpus delicti.*

Into this class fall stains, weapons, documents, poisons, counterfeit money, dusts circumstantially associated with crimes, and in fact traces of every kind found on the scene of the crime or elsewhere which throw light upon its commission. We shall, of course, deal only with those materials which are amenable to chemical examination.

THE CHEMICAL EXAMINATION OF BLOODSTAINS

Stains upon clothing and elsewhere if suspected to be those of blood must be tested. It is important to note that bloodstains cannot necessarily be recognized by their appearance. They may be black, green, or brown in colour. For the preliminary tests very small quantities of the stain should be used. It should be mutilated as little as possible in securing the sample to be tested. A general method is to moisten a piece of filter paper with distilled water and apply it to the stain.

The Benzidine Reaction.—The reagent is prepared by filtering a saturated solution of benzidine in acetic acid to which a few drops of an 0.1 N solution of sodium perborate have been added. The reagent should be freshly made up in small quantities for each test. A few drops of the solution are added to the aqueous extract of the stain on the filter paper. If blood is present a blue or green colour develops. The test, however, is not specific.

The Guaiac Resin Reaction.—The reagent consists of a filtered solution of the resin in alcohol to which have been added a few drops of ozonized turpentine. The test is carried out on blotting paper in the same way as for the benzidine reaction. A blue colour develops after a few seconds if blood is present.

The Leuco Malachite Reaction.—This test already noted (*Medinger. Rev. Inter. de Crim.*, 493, 1931) is the most delicate known for blood. One gram of the leuco base of malachite green is dissolved in 100 cc. of glacial acetic acid and 150 cc. of water. The stock solution must be kept in a dark brown bottle and it must be tightly sealed. It will then keep indefinitely. For the actual test a mixture in the ratio of 4 to 1 is made with the reagent and a 1 % solution of hydrogen peroxide.

The most suitable method of performing the test is to add a small fragment of the stain to a drop of the reagent on a porcelain tile. The mixture should then be macerated with a glass rod. A dark green coloration will develop at once if blood is present. On standing for a minute the coloration becomes bluish-green. Another method is to transfer the fragment to a piece of filter paper and add a drop of the reagent on one side so that it comes in contact with the fragment as it spreads.

For very minute stains, moistened filter paper can be applied and a drop of the reagent added. The test is, in fact, so sensitive that it will detect the presence of blood in circumstances where no stain is visible. In the case of motor accidents it is quite common to find no visible traces in the supposed origin of impact. In these circumstances pieces of filter paper moistened with the reagent are applied to the surface to be tested at all suspected points. If the minutest trace of blood is present the reaction will be positive.

The extreme delicacy of this test makes it necessary to ensure that all apparatus is chemically clean. Minute traces of blood from previous tests may otherwise lead to error. The reaction should be definitely positive and should in all cases show the colour change on standing.

Teichmann's Reaction.--This relies upon the microscopical identification of haemin crystals. A portion of the stain is mounted with water upon a microscopic slide and the liquid evaporated over a water bath. A cover slip is then placed over the residue and a drop of glacial acetic acid run in under the slip. The mixture is again evaporated to dryness. This operation is repeated three times. The residue is then examined microscopically. Coffee-coloured crystals of haemin will be observed if blood is present.

Strzyzowski Reaction.—This relies upon the formation of the bromo- or iodo-hydrate of haematin, the formation of the iodo-hydrate being a modification which has been devised by Locard. Locard's method is to mix sodium bromide or iodide with the aqueous extract of the suspected stain on a microscopic slide and evaporate the mixture to dryness with very gentle heat. The cover slip is then placed in position and a drop of a mixture of alcohol, water and glacial acetic acid in the proportions of 1 : 1 : 1 is run in beneath the slip. The extract is again evaporated slowly. Large crystals of the bromo- or iodo-hydrate of haematin are observed if blood is present.

The classical method is to treat the stain with the following mixture :

	Parts
Alcohol	1
Distilled water	1
Glacial acetic acid	1
Hydriodic acid	3

The method of performing the test is the same as that of Teichmann's reaction.

Confirmation of Results

In so important a matter as the identification of blood, it is essential that confirmation of all results should be obtained. It is extremely unsafe to rely upon unconfirmed results. Lucas (*Forensic Chemistry and Scientific Criminal Investigation*) recommends the benzidine reaction as the most useful preliminary test. He has stated (*p.* 32) that " In no case has the presence of blood ever been found after a negative benzidine reaction." In our experience the same is true in regard to the leuco-malachite reaction. In regard to confirmation, if the benzidine and leuco-malachite reactions are positive, one of the micro-chemical tests, Strzyzowski's reaction as modified by Locard, should be applied. If this is also positive it may be safely assumed that the stain is one of or actually contains blood.

Method of Beam and Freak

This is a modification of the haemin test strongly recommended by Lucas (loc. cit., *p.* 36), who has wide experience in the examination of blood. These authors (*Bio-Chemical Jour.* 9 (1915), 161–70) describe the test as follows :

> A small quantity of the suspected material is placed at the bottom of a flat arsenic sublimation tube about 6 by 3 mm. and 35 mm. long. A thin round ignition tube will answer if no flat tube is procurable, but for examination under the microscope the flat form is obviously better. A few drops of acetic acid containing from 0·01 to 0·1 per cent sodium chloride are added and a very fine cotton thread adjusted so that its upper end is near the top of the tube and the lower end reaches to the bottom of the liquid. The thread should be everywhere in contact with the tube, to which it adheres readily by being moistened with the liquid. The adjustment is readily made by means of a glass rod one end of which is drawn out for the purpose. The tube is now placed in a rack, or supported by forcing its base into a small blob of plasticine, and allowed to remain until crystallization has taken place.

> Before placing the thread into position, the solution of the blood may be aided, if desired, by cautiously heating the tube over a small flame, loss of the liquid by explosive boiling being prevented by holding the finger tightly over the mouth of the tube.
>
> While such heating appears rarely to be essential, the long contact with the acid in the cold sufficing for solution in practically all cases, it is nevertheless advisable in that it gives at once an indication of the strength of blood solution obtained. For the best results this should be quite weak.
>
> The clear liquid, filtered by its passage through and along the thread, is slowly drawn up, by capillary action, to the mouth of the tube. Under these conditions evaporation takes place so slowly that, even when the temperature of the atmosphere is above 38·C., it is complete (if the tube is held in an upright position) only after 12 to 24 hours or more. The rate of evaporation is readily controlled, within wide limits, by altering the dimensions of the tube and the angle at which it is supported.
>
> The crystals usually begin to appear, on or near the upper half of the thread, and of sufficient size to be distinguished with a power of 75 diameters, in about an hour; and they ultimately become so large that, in place of requiring a magnification of 250 to 300 diameters, as usually recommended, they may readily be seen with one of 25 diameters or even, in many cases, with a good hand lens. The crystals are best viewed against a dull white background. A piece of white paper is suitable.
>
> The extraordinarily large size of the crystals is due, in great part, to the slow evaporation of the liquid; but it is also a result of the removal, by the thread, of the interfering action of the blood albumin on crystallization. Examination of the thread at the end of the experiment shows that the soluble, non-crystallizable constituents of the blood are carried to its upper end, and that the maximum growth of haemin crystals is found lower down.
>
> If the solution is sufficiently weak, the first crystals form at the point of greatest concentration—the upper end of the thread; but as the albuminous matter accumulates these cease to grow and the largest and most numerous crystals are found, later, about midway down the tube.
>
> For the best results the following precautions should be observed:
>
> The tube should be thoroughly clean and dry. It is best cleaned by swabbing out successively with acetic acid, water, and alcoholic soda, followed by thorough rinsing with distilled water and drying on a hot plate.
>
> The thread should be clean and as fine as can be obtained. A good plan is to take No. 80, " six-cord sewing machine cotton " and to untwist it, using one of the " cords " for the test.
>
> The solution of the blood in acetic acid should not be concentrated, but very weak. The liquid should only be faintly pink. This ensures large crystals and clean fields.
>
> If the method is to be applied experimentally to fresh blood, the latter must be completely dried before the addition of the acid, and especial care should be taken to work with very dilute solutions.

The large-sized crystals found in this test to which the authors allude make the results particularly easy to interpret. The disadvantage is that it takes some time to carry out. It is a very valuable confirmatory test which should not be neglected if opportunity exists to make use of it.

Interfering Agents

It is important to ensure that the crystals formed in the haemin and haematin reactions are of a brown colour. Inorganic salts may assume a form which will be confused with those of the true blood reaction. They are, however, colourless. Indigo, often associated with textile fabrics on which stains are found, forms crystals somewhat resembling haemin or haematin crystals. They are, however, blue. Iron and calcium salts interfere with Teichmann and Strzyzowski's reactions. Very old bloodstains, and those which have been treated with soap or alkalis sometimes give uncertain results.

THE EXAMINATION OF SPERM

Sperm stains are recognizable by the starched appearance which they give to fabric and to the geographical formation of the borders of the stain. The appearance, however, is not specific, and does not serve to identify the origin of the stain. Fresh stains have a characteristic smell which can be readily identified. The dry stain has as a rule no smell, or if it has, it is characteristic of urine.

Florence Reaction.—There is no specific chemical test for seminal fluid or stains. The Florence reaction must be applied. 1·5 grams of potassium iodide and 2·5 grams of iodine are dissolved in 30 cc. of distilled water. This must, of course, be done with the usual precaution of dissolving the iodine first in a concentrated solution of the potassium iodide. A small portion of the stain is mixed with the reagent on a microscopic slide and the reaction watched under the microscope. The formation of brown rhombic crystals occurs in the presence of sperm. Pus, blood, urine, and saliva also respond to the Florence reaction.

The only specific test for sperm is the microscopic detection of spermatozoa. The identification of spermatozoa should, however, on no account be attempted by a chemist who has not specialized in such work. Several cases are on record where vaginal fluids containing flagellate protozoa have been reported to contain spermatozoa. A physician specialized in such examinations must make the report.

It is, however, often desirable to stain the preparation. Spermatozoa if treated with silver nitrate which is afterwards reduced are stained black by the reduced silver salt. A portion of the stain is soaked in a 3% solution of silver nitrate for six hours at a temperature of 50°C. The stain is then washed thoroughly in one of the following solutions. (*See p.* 10.)

Water	100	Water	100
Formalin	5	Hydroquinine	1·6
Pyrogallic acid	4	Sodium sulphate	10
Pyridine	8	Pyridine	8

The stain is then again washed for half an hour in water. A portion of the stain is then carefully transferred to a microscopic slide and mounted in the ordinary way. Spermatozoa are much more readily identified when stained in this way than when they are unstained.

THE MICRO-CHEMICAL EXAMINATION OF OTHER STAINS

Classification of Stains.—Stains, like dusts, are of very variable types, but a general discussionof them is necessary because their nature may affect the chemical methods of examination applicable to them.

First, stains, more commonly than dusts may consist, for practical purposes, of a single substance and when they are mixtures they are seldom so complex as dusts. Examples of simple stains are blood, wax, sperm and chemical stains consisting of a single substance.

Secondly, there are stains which are chemically speaking mixtures. Examples are stains of mud, paint, ointment, and many occupational stains of mixed composition.

Thirdly, there are stains which are mixed fortuitously with some substance which may be of particular evidential value such as particles imbedded in blood or other substance which upon hardening, clotting, or in some other way may occlude material not inevitably associated with the stain as such. These materials are, in effect, dusts. Examples are stains of gome which may contain metallic particles if the stain is associated with the clothing of mechanics.

Location.—Stains may, of course, be found anywhere, but a very large proportion of those of criminalistic importance are found upon clothing or associated with textile fabrics. The significance of this is that the removal of the sample from a hard smooth surface does not usually present much difficulty, but the case may be otherwise if the stain is associated with a textile fabric. What is required is a sample of the stain free, as far as possible, from admixture of material with which the stain is associated. Solution of the sample is generally the most satisfactory way of dealing with it, but unless its composition is broadly known, this may present difficulties.

Search for and General Identification of Stains.—Stains are not necessarily recognizable by ordinary inspection. Bloodstains for instance are not always detectable as such since they are not necessarily of characteristic colour. Stains, however, produced by waxes or oils can generally be identified and those of such substances as tar, paint and sealing wax. It may be necessary to examine the stained material with ultra-violet light. As a result of this treatment hidden stains which reflect ultra-violet rays and fluoresce may reveal their presence, or they may absorb the rays and thus show as dark patches against a fluorescent background with the same result. In some cases the nature of the fluorescence may give a clue to the nature of the stain.

Preparation of Stains for Examination.—There are certain general rules which should be followed. If the stain is on a hard surface not readily injured by mild instrumentation the stain can be removed dry with a knife or spatula. Care must be taken to avoid removal of the substratum. If there is danger of this the substratum must be cut out with the stain.

In the case, however, of textile fabrics it is not possible, as a rule, to deal with the stain in this way. Although stains of paraffin wax and other substances which solidify can sometimes be removed mechanically, it is generally necessary to dissolve the stain if a proper separation is to be effected. It should be noted here that whenever possible the stained area should be cut from the fabric and treated independently. It is hardly possible by methods of solution to deal with the stain in situ.

The first type of stain to which allusion has been made has been described as simple because it consists essentially of one substance. Its separation from the textile substratum therefore consists in treatment with an appropriate solvent. The type of treatment will depend upon some general indication of the nature of the stain. If there is no indication of this kind, it is necessary to proceed in the same way as in the extraction of dust. Micro-quantities of the sample are treated successively with water, alcohol, and a fat solvent for the purpose of ascertaining in which type of solvent the solution of the stain is complete or most complete. The sample is extracted first with water and the extract is evaporated to dryness. The alcoholic extraction is then made and also evaporated. Finally an extraction is made with ether or acetone. The evaporated extracts are carefully examined with a view to deciding which solvent is the most efficient.

The second type of stain, the mixture, is more difficult to deal with, but in this case, the same method of successive extraction can also be applied. All three solvents may, however, yield appreciable quantities of extract all of which will require independent examination. In the case of stains made by mixtures the insoluble matter from the extractions must also be examined. The insoluble matter which in all cases includes a certain amount of debris from the fabric itself may be as important for the purposes of identification as the extracts, or more so. This is not usually so in the case of simple stains which are likely to be either insoluble in all the solvents or completely soluble in one of them.

The third type of stain which may contain occluded matter of evidential value requires preliminarily different treatment. The scrutiny under ultra-violet rays should be of a very searching character.

The reason for this is that particles may, by reason of a differential fluorescent or absorbent effect, reveal their presence. If they can be located in this way or by ordinary micro- or macroscopic inspection an attempt should be made mechanically to remove them for independent examination. If this is not possible, the three-fold method of extraction should be applied as in the previous cases. In these circumstances particular attention is given to the insoluble matter which must be examined for particles which are recognizable as foreign both to the general nature of the stain and to the substratum. They are then separated and independently examined.

This technique is a satisfactory general method of preparing stains for chemical examination. But, as in the case of the methods applicable to dust, it must not be followed blindly as if supplied by nature ready made. Stains are of so variable a character and may differ so greatly in physical properties that no rules in regard to their treatment, however generalized, can apply without exception. It is for this reason that the application of a micro-chemical technique to preparations of this kind is so important since it generally gives considerable latitude for the application of alternative methods of attack. Properly applied on a micro-scale a scheme of this kind will give information upon which larger scale operations can be based, and the sample can thus be made available in a form which may make possible its complete examination.

Applications in Practice.—As in the case of dusts, it seems desirable that some examples from actual practice should be given which indicate the manner in which the general technique can be applied to the examination of stains of specific kinds, so that the special case can be considered in the light of the general technique.

Blood.—Owing to the extreme sensitivity of Medinger's reagent minute quantities of blood (as an example of a simple stain) can be identified. Even if the stain is too small to be detected by ordinary inspection the reagent can still be applied to suspected surfaces with positive results. A piece of filter paper is moistened with the reagent and applied to the suspected surface. If the minutest trace of blood is present it will react. Traces of blood upon the mudguards of motor cars suspected of collision with pedestrians have been identified in this way. This is an example of the solution of a simple stain undetectable by inspection, in the reagent itself. It is the equivalent of an aqueous extraction.

Candle Wax.—Wax stains or those of solid fats are usually identifiable in a general sense by inspection. Extraction with acetone ether or other solvent and evaporation of the extract separates them from extraneous non-fatty material and thus assists identification. Candle wax can often be identified with a high degree of probability by mere inspection.

An interesting crystallographic method of identifying individual candle wax has been described by Dangl (*C.r. Acad. Inter. de crim., Vienna*, Oct., 1930). He has shown that if the wax is melted under carefully controlled conditions of temperature and then cooled, it develops a characteristic structure which is clearly shown microscopically under polarized light.

A small quantity of the wax is melted exactly at the temperature of fusion upon a microscopic slide, the preparation being protected by a cover slip. On cooling the wax is examined microscopically with polarized illumination. As a result of the treatment, highly characteristic crystalline structures are observed which serve to distinguish different samples of wax.

The method is particularly successful with the cheaper forms of wax containing derivatives of fatty acids which raise the melting point.

The treatment produces conditions analogous to those which obtain when a metallic alloy is cooled and passes from the dystetic to the eutectic state. As with metallic alloys well-defined structures result.

This is an example of the treatment of a simple stain with an appropriate solvent after its general nature had been identified.

The method of identifying the individual wax is of great value because it is often important to determine if a stain of this character corresponds with the wax of a particular candle. It is a micro-method which can be applied to very small quantities of material. In carrying out the test, however, it is essential that the melting temperature should be rigidly controlled by means of a thermopile, and that the cooling should also be carried out under standardized conditions. The weights of the samples to be compared should closely approximate.

It seems probably that this method of identification could be adapted for the examination of other types of wax.

Paint Stains.—These stains are examples of mixtures which require more elaborate treatment. From the point of view of identification the recovery of the pigment is more important than that of the vehicle. The stain can be digested in acetone which dissolves the vehicle, and loosens the insoluble pigment. Lengthy digestion in the solvent may be necessary, and maceration of the material to loosen the insoluble matter. The soluble portion is, however, retained for independent examination. It should be noted if the acetone extract is coloured. This will indicate the presence of an organic pigment.

The insoluble pigment is examined micro-chemically for appropriate bases and acid radicles. Bases such as lead, zinc, barium iron and mercury may be found and sulphates, carbonates and dichromates. The colour of the pigment will often give an indication of its composition.

Stains Containing Occluded Foreign Matter.—It has already been indicated that it is essential, where occlusion is suspected, if possible to isolate the occluded particles and examine them independently.

The best example of this type of stain is that of mud. Mud frequently contains particles of evidential value which are not amenable to chemical examination but which have to be separated from the material by the help of chemical methods. Mud stains should be macerated with water so that all the insoluble matter is mechanically removed. The aqueous extract is separated by one of the methods of micro-decantation already described, and retained. An examination of the residue is then made with a lens or microscopically with low power. Vegetable fibres, seeds or anything obviously foreign to the soil as such must be mechanically separated and preserved for appropriate examination.

The aqueous extract is then evaporated to dryness and the residue (if an appreciable quantity is found) examined for any special characteristics, the presence of crystals or amorphous matter which may make advisable a more complete examination. If this is not undertaken the residue and the insoluble matter are united so that an analysis of the soil can be made if this is necessary. In certain cases a micro estimation of iron, aluminium, calcium and silica may be useful for comparison with a sample taken from the locality whence it is suspected the mud-stain may have emanated.

In cases of stains upon mechanic's clothing a search is made for particles which may consist of finely divided metal. Whether these are discovered or not the stain is extracted with a fat solvent and the residue examined. Metallic particles are very frequently isolated in this way, and can be independently examined.

These are examples of the practical application of the general methods described for the examination of stains. In order successfully to deal with stains in general considerable judgment and experience are required. This is especially true in connection with the isolation and examination of occluded and extraneous particles. In many cases these will not be amenable to chemical examination and will, in fact, have to be investigated by those with appropriate qualifications to deal with them. The chemist, however, must be able to recognize entities of this kind so that he does not apply any method to the preliminary examination of the stain likely to interfere with any non-chemical examination which may be necessary. Where necessary he must seek the help of an appropriate expert.

CHAPTER IV

FIREARMS AND EXPLOSIVES

(a) The Chemical Examination of Firearms

General.—The chemical examination of the products of explosion in the barrels of firearms frequently produces evidence of considerable value from a forensic point of view. In cases of shooting, therefore, when the discovery of the firearm places it in the category of *corpus delicti*, a chemical examination of the contents of the barrel must always be made. In this connection, however, as in many others, the results must be interpreted with caution. Hans Gross, for example (*Criminal Investigation*) in discussing the interpretation of the results suggests that the period at which the gun was fired can be determined within very narrow limits if the products of explosion have been identified. His conclusions, however, require modification, and positive conclusions should not be founded upon facts which experience has shown do not in all cases admit of precise interpretation. On the other hand, the presence or absence of certain substances can be correlated with the time factor within certain limits.

Types of Powder.– There are two forms of powder commonly used in cartridges, namely, black and smokeless. They are of very different composition and the products of their decomposition vary greatly. It is therefore of importance to know the type of powder which has been used in the case under examination. In the absence of other evidence it may be possible to decide this from the chemical examination of the residues.

Military rifle ammunition usually contains smokeless powder. Sporting ammunition either black or smokeless powder. Automatic pistols and revolvers are generally loaded with smokeless powder, but the ammunition may contain a mixture of black and smokeless powder.

Composition of Black Powder.--Black powder is essentially the classical gunpowder which does not vary in composition from early types. It consists of charcoal 15 %, potassium or sodium nitrate 75 %, sulphur 10 %. These proportions are approximate, but in good powder should not vary more than ± 1 %. Modern gunpowder is very uniform in composition, but the purity of the constituents varies as do the proportions of the ingredients within narrow limits.

Products of Explosive Decomposition.—As is generally known most explosions result in the formation of large quantities of gas.

The gases produced by the explosion of black powder are carbon dioxide, carbon monoxide, hydrogen, methane, nitrogen, and hydrogen sulphide. The following solid substances are also decomposition products. Potassium carbonate, potassium sulphate, potassium sulphide, potassium thiocyanate. With the exception of the hydrogen sulphide the gases formed have little forensic importance. It is the identification of the solids which provides evidence of value.

As Fleury, Silvera and others have noted, explosive decomposition is never complete. Traces of free sulphur remain and small quantities of unburnt charcoal. Chavigny has stated that traces of potassium nitrate may remain undecomposed. Lucas, however (*Forensic Chemistry, p.* 202), does not confirm this observation. The present author has never discovered nitrates among the decomposition products of explosion of black powder.

From a forensic point of view only those products of decomposition are important which, if identified, serve to indicate the time at which the shot was fired. The substances for which tests should be made are sulphides, sulphates, thiosulphates, thiocyanates, iron (ferrous and ferric), nitrates, nitrites and alkalinity.

Lucas (*Forensic Chemistry, p.* 205, *et seq.*) has carried out an interesting series of experiments relating to the composition of the products of explosions in the barrels of firearms at known periods after firing.

He has found that hydrogen sulphide will persist in the barrel of a weapon of which the breech has been closed for two to three hours ; if the breech is open, however, the gas disappears in from one to five minutes.

The greater part of the sulphides has decomposed in from four to five hours, but traces have been observed to remain for ten hours.

Sulphates are present at all periods but they increase in quantity with time owing to the oxidation of the sulphides.

Thiosulphates are one of the decomposition products of the sulphides. Thus they appear only when the sulphides have decomposed. It would appear that they result from the oxidation of the potassium sulphide.

Thiocyanates are occasionally found.

Ferrous iron is always present in the residue, but it undergoes slow oxidation. It would appear that ferric iron is first found after twenty-eight hours. It is not, however, found in a soluble form earlier than after thirty-three days. Varying conditions such as those of atmospheric moisture influence these reactions.

Nitrites are never found less than four hours after the shot was fired. The presence of sulphides interferes with the formation of nitrites so that their appearance is contemporaneous with the decomposition of the sulphides.

These interesting experimental results confirm and considerably supplement the findings of Chavigny (*L'expertise des plaies par armes a feu, Paris*, 1913).

Smokeless Powders.—These powders consist essentially of nitro-cellulose which may exist as the sole ingredient or mixed with nitro-glycerin. Other varieties contain vehicles such as mineral jelly with the addition of potassium or barium nitrate. Macerated wood is also an occasional ingredient.

The products of explosive decomposition are gaseous and solid, the gases being mainly carbon dioxide, carbon monoxide, nitrogen and hydrogen. The solid products are nitrites, nitrates, and sulphates. Sulphides are generally absent.

The condition of the barrel from which a cartridge containing smokeless powder has been ejected differs greatly from that produced by black powder. In the first place the fouling of the barrel is less marked and is much lighter in colour.

An aqueous solution of the contents of the barrel is either colourless or slightly brown. Nitrites may be and generally are present. Black powder on the other hand produces a much darker solution in which nitrates are seldom if ever found. The reaction of the aqueous solution of the residuum of smokeless powder is neutral whilst that of black powder is alkaline.

Variations in Composition.—Smokeless powders vary greatly in composition so that the products of their explosion also vary. It is not, however, generally possible to base any conclusions of a precise nature upon such variations. The quantity of nitrate found, however, is much greater in some cases than in others. This might exclude certain powders known to produce only small quantities of nitrates on explosion. More specific evidence is supplied by the presence of barium or chromium in the residues. These more unusual constituents may give an indication concerning the type of powders used.

Examination of the Barrel Residue.—The appearance and smell must be noted as soon as the firearm is received. Before the breech is opened a test should be made for hydrogen sulphide with lead test paper in the usual way. With the breech closed the paper will naturally be applied at the muzzle as close as possible and should be retained there for not less than a minute.

If the reaction is negative, the breech should be opened and a current of air blown through the barrel. The breath should not be used. A rubber bulb with a short nozzle is the simplest method of injecting air.

The barrel is then rinsed with boiling distilled water. This can best be done with a wash bottle fitted with a very fine jet. The firearm should be supported with the barrel in a slanting position and with the muzzle placed over a small beaker to catch the liquid. Small washings should be used and a rotary motion given to the nozzle of the wash bottle. The total volume should not exceed 25 cc. After this first washing the washings should be returned through the barrel, pouring through the whole volume as quickly as possible. This operation should be repeated a second time. By this means an efficient washing of the barrel is assured.

The colour, appearance, and smell of the solution must be noted. The reaction to phenolphthalein should also be examined. Alternatively, the approximate hydrogen ion concentration may be determined by means of a universal indicator.

The solution is then filtered and the appearance of the residue noted. The filtrate is treated as follows : (1) If alkaline, a portion of the filtrate should be neutralized, (2) A further portion should be acidified with hydrochloric acid free from iron.

(1) **Sulphides.**—Solution (1) should be tested for sulphides with lead acetate.

(2) **Ferrous and Ferric Iron.**—(Solution 2) The most satisfactory test for ferrous in the presence of ferric iron is the *αα′* dipyridyl reaction. The pH of the solution should be slightly on the acid side (up to 3·5). The reagent is used in aqueous solution.

Potassium thiocyanate may be used for the identification of ferric iron. If a more delicate test is required the 7-iodo-8-hydroxyquinoline-5-sulphonic acid (ferron) in aqueous solution may be used. It has been stated (*Yoe*, *J. Amer. Chem. Soc.*, 1932, 54, 4139) that this reagent will detect concentrations of ferric iron of the order of 1 in 10,000,000. It is in any case more sensitive than the classical test with potassium thiocyanate. The test solution should not exceed pH 3. The thiocyanate test is, however, generally sufficient.

Sulphates.—The classical test with barium chloride should be used. The portion used should be that faintly acidified with hydrochloric acid.

Nitrates.—Lucas (*Forensic Chemistry*, 211) has pointed out that the tests with brucine or the 1–4 diphenyl-3-5 endanilo-4-5 dihydro-1-2-4 triazole are unsatisfactory owing to the interference of ferric salts, nitrites, and other substances which may be present in the residues of powder. This author recommends the classical " black ring " test or that with phenolsulphonic acid and ammonium hydroxide.

The diphenyl-benzidine test is, in our experience, also satisfactory. A 0·02% solution of the reagent is used in pure sulphuric acid. 2 cc.

of pure sulphuric acid are added to every 1 cc. of the solution to be tested. 1 cc. of the reagent is then added. After standing 24 hours a blue colour develops in the presence of nitrates. It should be borne in mind, however, that the " black ring " test is, with careful manipulation, very sensitive, and it can be carried out on a very small quantity of solution.

Nitrites.—Nitrites may be identified as follow. A solution of sulphanilic acid is prepared by dissolving 0·8 gram of the acid in 100 cc. of distilled water. The second reagent consists of a solution of 0·5 gram of naphthylamine hydrochloride in a 0·8 % solution of hydrochloric acid. To 10 cc. of the solution under test 0·2 cc. of the solution of sulphanilic acid are added followed by 0·2 cc. of the solution of naphthylamine hydrochloride. The mixture should be stirred and let stand for half an hour. A pink coloration indicates the presence of nitrites. (*Lucas and Barral.*)

Potassium.—A 1 % solution of hexanitro-diphenylamine in 0·1 N sodium carbonate may be used to identify potassium (*see p.* 31). Other substances likely to be present do not interfere, but if ammonium salts are present they must be removed.

Interpretation of the Results.—It is necessary to repeat that the results of the analysis must be interpreted with great caution. In preparing the report, the chemist should state the findings of the analysis precisely and he should then indicate the probable conclusions to be drawn. On no account should any dogmatic statement be made. If the examiner is in doubt it is preferable to withhold judgment altogether than to draw too positive an inference from the evidence supplied by the analysis. The following points, however, will serve as a guide.

Smell.—If the smell is marked it is probable that the firearm has been very recently fired. It is not generally possible to identify the smell as positively resembling hydrogen sulphide although some examiners profess to be able to detect this in a recently fired firearm. The smell differs with black and smokeless powder and the odours can be distinguished by an experienced nose. (*Chavigny, Supra.*)

Appearance of the Deposit.—This requires guarded interpretation. In general the deposit left by black powder is much darker than that of smokeless powder. Söderman and Gerard have noted that whilst a black powder freshly fired is black or dark grey in colour, it may become light grey or even white with the lapse of time. If therefore the deposit smells very faintly, and is white, the charge may have been one of black powder. On the other hand, a strong smelling white deposit is most probably smokeless powder. It is not possible to identify a mixed powder residue by inspection and/or smell.

Hydrogen Sulphide and Sulphides.—If the smell of the residue resembles hydrogen sulphide, the firearm (a) has been very recently fired and (b) the charge consisted of or contained black powder. If an abundance of sulphide is observed, the gun was recently fired. If traces are present it was probably discharged more than five hours before examination. This, however, refers to black powder only. Sulphides are not found in the residue of smokeless powder.

Alkalinity.—An alkaline residue indicates that the original charge was one of black powder. The alkalinity varies inversely as the time, but no conclusion as to the time of firing can be drawn from this fact.

Sulphates. — Sulphates are always present in black powder residues and may be present in smokeless residues. Sulphides vary inversely and sulphates directly as the time. Sulphates are present at all stages in the residue. Although their quantity increases with time at the expense of the sulphides no positive conclusion can be drawn as to the time of firing.

Thiosulphates.—Thiosulphates are occasionally found in the residues of black powder but not in those of smokeless powder. Being formed by the oxidation of potassium sulphide they are not present in the early stages. No conclusion as to the time of firing can, however, be drawn from their presence.

Thiocyanates.—Lucas states that thiocyanates are occasionally found in the residues. No conclusion can be drawn from their presence.

Nitrates.—Nitrates if present to a very marked degree indicate that the residue is one of smokeless powder. Nitrates are seldom if ever present in the residue of black powder. The quantity may vary from a trace to that sufficient to produce a marked reaction.

Potassium and Sodium.—The presence of potassium does not directly indicate what type of powder was contained in the charge. Its absence, however, shows that the charge is probably one of smokeless powder since potassium is normally present in black powder. But it must be noted that black powder is occasionally made with sodium nitrate. The absence of both sodium and potassium shows that smokeless powder was used.

Other Bases.—Barium, strontium and chromium are sometimes found in the residues of smokeless powder. The presence of constituents of this type may be a useful guide to the identity of the powder, and may provide important evidence of a negative character. It will, for example, explicitly exclude a number of powders known not to contain the constituents found.

These notes will make it evident that much useful information can be gathered from the examination of the residues found in the barrels of firearms provided due care is taken not to exaggerate the evidential significance of the facts. It will be clear, however, that the residue of smokeless can be distinguished from that of black powder, and that in certain circumstances chemical tests supply evidence of the time at which the shot was fired. Special types of smokeless powder may be identified by reason of the presence of special constituents. These general inferences, often of value in themselves, can in most cases legitimately be drawn.

(b) The Chemical Examination of Bullets

The examination of bullets may give important information as to their identity and origin. Bullets are of two general types. (1) Those of uncoated lead and (2) those sheathed with a harder metal which covers a lead core. Both the lead itself and the coating material may vary considerably. Whilst the lead is of the ordinary commercial type, the impurities found in it, such as arsenic, antimony, and tin, vary often to a sufficient extent to make identification possible.

Coatings are of various types. They may consist of copper-nickel, soft steel, copper-zinc or copper alone. British rifle bullets are coated with an alloy of 80 % of copper and 20 % of lead. American coating consists of 90 % of copper, 8 % of zinc, and 2 % of tin. French bullets are frequently copper sheathed. An analysis of the bullet will thus give a clue to its origin. In any case, comparison of the analysis with that of unfired ammunition may be the means of tracing the bullet to its source.

Preliminary Examination.—The first and most important operation is to weigh the bullet accurately. Bullets show great variations in weight but the weights of the bullets of the same type are constant within fairly narrow limits. Variations of the order of ± 0·4 gram may be found in bullets of the same type, so that small differences are not of much evidential value.

When the weight has been determined, reference should be made to the manufactuers' catalogues. These generally record the maximum and minimum weights of the bullets so that an indication of the origin of the bullet may be obtained from the weight alone. On the other hand, the weights of bullets of different makes often lie close together and caution must be observed in interpreting evidence of weight. As a sorting test it may, however, be of great value.

Analysis.—Determination of Lead.—Lead can be estimated n the form of sulphate by solution of a weighed portion of the bullet n sulphuric acid to which has been added ammonium sulphate to void the precipitation of the tin. The disadvantage of this method is hat the results tend to be too high if tin is present owing to the formation of the insoluble stannic sulphate. If tin is absent, the method is satisfactory.

In the author's experience the volumetric estimation of the lead oxalate is the most convenient. The weighed portion is dissolved in nitric acid. It is then exactly neutralized with sodium hydroxide. Oxalic acid is then added in excess (ammonium oxalate must not be used). The precipitated lead oxalate should be allowed to stand for two hours. It is then filtered. The precipitate is washed with hot water and dissolved in very dilute nitric acid. Sulphuric acid is then added and the solution titrated with 0·1 N potassium permanganate. 1 cc. of potassium permanganate = 0·01035 gm. Pb. and the equation is :

$$2KMnO_4 + 5PbC_2O_4 + 8H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5PbSO_4 + 10CO_2 + 8H_2O$$

Antimony.—If antimony is present without tin the weighed sample should be dissolved in strong nitric acid and the solution diluted with water. The antimony remains as an insoluble residue of hydrated Sb_2O_3. The oxide is filtered off, ignited after separation from the filter paper. Before ignition it should be moistened with nitric acid and gently heated before burning.

Antimony and Tin.—If these metals are present together the solution from which the lead has been removed should be treated with hydrogen sulphide. Both antimony and tin are precipitated. The precipitates are dissolved in a 10% solution of hydrochloric acid which must be heated until the mixed sulphides are dissolved and the hydrogen sulphide completely expelled. Boiling must be avoided or antimony will be lost.

The solution is then diluted so as to reduce the acidity to about 1%. It is then titrated with 0·05 N potassium permanganate.

$$10SbCl_3 + 16HCl + 2KMnO_4 = 10SbCl_4 + 2KCl + 2MnCl_2 + 8H_2O$$

To estimate the tin, the same solution should be evaporated to about 150 cc. The solution is then reduced by the addition of about 50 cc. of strong HCl and some fragments of pure iron and a trace of metallic antimony. It is essential that the tin should be completely reduced to stannous chloride. To ensure this the solution should be transferred to a second flask containing iron and a little hydrochloric acid, the reaction having been first allowed to continue for two minutes. The solution is then boiled until the iron is dissolved and while cooling the flask must be connected with a carbon dioxide generator. The titration must also be carried out in an atmosphere of CO_2. It is effected with 0·1 N iodine solution using starch as indicator.

$$SnCl_2 + I_2 + 2HCl = SnCl_4 + 2HI$$

Iron, lead, and antimony do not interfere with this estimation. Copper is unobjectionable if less than 3 % is present (*Scott*). Arsenic, however, must be removed. The separation can be effected by distillation owing to the volatility of arsenic trichloride.

Nickel.—This metal can be conveniently determined with dimethyl-glyoxime. Lead, copper, and tin must, however, first be removed with hydrogen sulphide. The filtrate from which the hydrogen sulphide has been removed should be nearly neutralized. It is then boiled and a 1 % solution of dimethyl-glyoxime in alcohol is added. A brilliant red precipitate $(C_4H_7O_2N_2)_2Ni$ is formed. It is filtered through a tared Gooch capsule, thoroughly washed, dried at 110°C. until constant in weight. The complex contains 20·31 % of nickel.

Interpretation of Results.—The interpretation of the results of the analysis is straightforward. The analysis is undertaken either (1) to compare it with that of a bullet of known manufacture, or (2) to compare it with ammunition found in possession of a suspected person. In these circumstances either the analyses will agree or they will not. If they agree there is strong presumptive evidence which may amount to a certainty that the bullets are of the same origin. Conversely, the negative evidence may be equally conclusive. There may be certain circumstances in which the bullets of differing origin agree fairly closely, but in general if it can be shown that, say, three constituents of two bullets are identical quantitatively, their identity is established.

(c) The Chemical Examination of Explosives and Explosions

This type of examination comes down in practice to being one of exploded or unexploded bombs of a certain type. Until recently such destructive instruments were not commonly met with in this country in connection with criminological enquiries. Recent affairs in England have, however, brought the question into prominence.

For forensic purposes bombs are of two general types, the military and the chemical. If as occasionally happens a military bomb is associated with a crime, it may be brought to the laboratory for examination. Only in exceptional circumstances should the chemist attempt to deal with this kind of bomb. He should refer the matter to an ordnance officer with experience in military bombs if one is available. Special precautions are necessary in opening military bombs. Thus the intervention of an expert is desirable.

Chemical bombs are of an entirely different type. Essentially they consist of an explosive mixture in which is imbedded a glass or other vessel containing strong acid. The explosion results when the acid comes in contact with the mixture. There are different ways of effecting this. The simplest is that in which the acid container is open, and the acid removed from it by some sharp movement. This is the crudest form and can only be used in small bombs which are thrown. There is a second type in which the glass container is very thin but closed. It breaks upon impact and thus explodes the mixture. This type of bomb must also be thrown.

The more elaborate type of " time " chemical bomb includes clockwork mechanism which operates a falling weight. This weight breaks the glass container and so explodes the bomb.

A third type has its timing adjusted in a different way. The acid-containing vessel consists not of glass but of some material more or less slowly attacked by strong acid. The time required by the acid to disintegrate a material of given quality and thickness is determined empirically. A container is then chosen of such a quality as to release the acid in the required time. Rubber is the material usually employed.

Preliminary Examination of Unexploded Bombs.—The very greatest care should be taken in examining and handling an object suspected to be an unexploded bomb. This warning might appear to be unnecessary, but it is not so in fact. It must be noted in the first place that a chemical infernal machine is not necessarily recognizable as such. Any kind of innocent-looking container may be used. Such articles as petrol cans and paint pots have been used for the purpose. In many cases indeed receptacles of this kind are deliberately chosen by reason of their unsuspicious appearance. Secondly, even trained individuals are sometimes extremely careless, so that the injunction quoted in one textbook that a suspected bomb " should on no account be shaken, inverted, or dropped upon the floor," is not so unnecessary as some might suppose. In one case within the author's own experience, an unexploded bomb contained in a paint pot was left on a laboratory bench for a few moments by the examiner without any warning notice attached to it. It was handled by an assistant unaware of its nature. The bomb exploded, part of the room was severely damaged and the assistant injured.

Before any attempt is made to open the bomb, it is advisable to take a radiograph of it if this is practicable. This will generally give an indication of the disposition of the contents, and what is most important the position of the glass or other vessel in which the acid is contained. The most dangerous type of unexploded bomb is that which carries an indiarubber acid container. If this is suspected no attempt should be made to open it, and it should not, in fact, be taken to the laboratory at all. The only method to follow is to explode it in any open space and proceed to the examination of the products of explosion.

Bombs containing glass containers can generally be safely opened if proper care is used. It is necessary, however, to work with extreme caution and carefully to consider every step before it is taken. Any moveable parts of the bomb should be detached and in particular any clockwork mechanism if it is visible. The lid or cover should then be removed if possible or if none exists a suitable method of opening should be chosen. It is, of course, impossible to lay down rules. Alike in principle home-made chemical bombs differ greatly in manufacture. The only rule to follow is to make a careful examination and then cautiously to attack the weakest point if it is judged that that point is not connected with any kind of detonating mechanism. If the container is so solid that any great degree of force is necessary, no attempt involving force to open it should be made.

If it becomes evident from the examination that the bomb includes mechanism which operates a hammer or falling weight, steps should first be taken to disconnect this mechanism and make it harmless. Care must be used in this operation or a result contrary to the one desired may occur. It is generally possible, however, before anything else is done to interpose an obstruction between the hammer or weight and the object it is designed to strike.

When a bomb is opened, it will probably be found to contain a glass or other container filled with acid. This may be open or closed. If open the container should be stoppered before removal. Alternatively the acid vessel may contain a lead or iron weight which makes great caution necessary in removing it. The first step to take is to separate the acid container from the surrounding material. It may be possible to do this by merely withdrawing it, but if it is firmly imbedded this may be very unsafe. It is often preferable to remove the explosive material leaving the container isolated in this way. At this stage the examination of the contents can be safely attempted.

Examination of Exploded Bombs.—The chemist should visit the scene of the explosion and make a careful examination. He should personally search for and collect the debris, and preserve it in labelled bottles with a note as to the position of the fragments collected. This preliminary examination may be of very great value since it will indicate the extent and thus the force of the explosion, the nature of the bomb casing, and of the materials used as projectiles. The explosive mixture usually contains fragments of iron which, of course, fly in every direction when the explosion takes place. All these fragments should be collected and carefully scrutinized since their physical appearance may give some indication as to the nature of the bomb.

Composition of Chemical Bombs.—The substances used to make chemical bombs are not very varied. They consist generally of mixtures of picric acid and potassium chlorate or potassium chlorate and sugar. Sulphur is a more exceptional ingredient. There are, of course, special cases as, for example, when metallic sodium is used as a constituent. In this connection it is important to remember that an unexploded bomb must not be placed in water unless it is certain that it does not contain this metal. Potassium chlorate generally forms one of the main constituents and picric acid is commonly found. A mixture of potassium chlorate and sugar is the simplest to secure so that amateur bombs often consist solely of these constituents.

The acid used is generally sulphuric acid, but nitric acid may be employed in some cases. Hydrochloric acid is very seldom found and where a timed detonation depends upon corrosive effect it is less suitable than the more corrosive agents.

The Products of Explosion.—Chemical bombs when they explode are seldom completely decomposed. Traces and in some cases appreciable quantities of the reacting materials remain unchanged. If these traces can be identified very valuable evidence may be secured as to the composition of the bomb.

Traces of picric acid, for example, may remain undecomposed. An alcoholic extract of the residue should be made and the alcoholic solution evaporated to dryness. The residue is taken up in water. The simplest tests for picric acid are its characteristic yellow colour in aqueous or alcoholic solution, its power to dye wool intense yellow, its acid reaction to litmus paper, and bitter taste. If sufficient of the test material is available a few drops should be warmed with a saturated solution of potassium cyanide. A red coloration indicates picric acid.

In some cases, potassium chlorate may be found unchanged after the explosion. The normal product of chlorate explosions is chloride. A test must always be made for chlorides and if they are abundant potassium chlorate was probably originally present. This, however, does not necessarily follow since chlorides might have been present in the original mixture.

A test should always be made for sulphates. Their presence usually indicates that sulphuric acid was used in the bomb. This conclusion, however, must be drawn with reserve since sulphates as such may be, although they seldom are, constituents of the explosive mixture. Sulphates also result from the decomposition of elemental sulphur if the original mixture included the element.

Nitrates may be identified by the black ring test or as follows: The aqueous solution is neutralized with sodium carbonate and evaporated to dryness. The residue is then moistened with 0·2 cc. of phenol sulphonic acid and allowed to stand for a few minutes. The mixture is then diluted with a little water and strong ammonia is added in excess. A yellow colour indicates the presence of nitrates.

A test should be made for potassium with hexanitrodiphenylamine. Potassium is almost invariably present in chemical bombs, but potassium salts are not absolutely essential. The absence of this metal may be useful evidence of identification since chemical bombs without potassium salts are unusual.

Interpretation of the Results.—It is obvious that the results of the analysis can only be interpreted generally. The presence of nitrates, sulphates, or chlorides does not enable the examiner to draw positive conclusions as to the original combination in which they existed. But the presence of chlorides and potassium probably indicate that potassium chlorate was originally present. If nitrates are present without potassium, nitric acid may have formed part of the original bomb. If potassium and nitrates are present together no definite conclusion can be drawn unless sulphates are also present. If sulphates, nitrates, and potassium co-exist potassium nitrate and sulphuric acid were probably present. These general conclusions should be borne in mind, but they must not be regarded as other than provisional in the absence of confirmatory evidence.

Examination of the Bomb Fragments.—The fragments if analysed may provide valuable evidence. It is, of course, impossible to suggest a scheme of analysis since every case must be treated individually. The fragments will, of course, be metallic and on complete analysis may give an indication of the source of the container of the bomb. Pieces of drainpipe have, for example, been used as containers. The piping has ultimately been traced to its source by reason of the evidence of the analysis. In any case, a careful examination should be made of the fragments particularly as to their shape and size even if the analysis is not undertaken.

Examination of Suspects.—In no kind of enquiry is an examination of the suspect's person and clothing so important as in the case of bomb outrages. First, a mere inspection of the skin of the fingers may indicate that picric acid has been handled by reason of the characteristic staining. Secondly, the deposit under the fingernails should be minutely examined. Traces of chemicals in an unchanged state may be identified in this manner, and proof obtained that explosive substances have been handled. Thirdly, the dust on the clothing may contain traces or even sometimes an abundance of these chemicals. This evidence is obviously of first-rate importance and the more so if the results can be correlated with those secured by the examination of the residues of the explosion. It will be obvious, for example, that if an abundance of chlorides is found in the residue of an explosion, and that potassium chlorate is found in the clothing of a suspect, there is strong presumptive evidence to connect him with the manufacture of the explosive agent.

On the other hand, the examination of the clothing of the victim of an explosion may give information concerning the composition of the bomb. Lucas quotes a case of a policeman injured by an explosion whose white tunic was stained yellow with picric acid at the place where a fragment of the bomb struck him.

CHAPTER V

THE CHEMICAL EXAMINATION OF QUESTIONED DOCUMENTS

(a) Constitution of Inks

General.—Whilst chemical examination of documents is not the only type of examination applicable to them, it forms an increasingly important part of any enquiry relating to a questioned document.

It is essential to remember that from a forensic point of view documents other than those suspected of being forged may have to be examined. There is hardly any kind of criminal enquiry which may not require the examination of a document or documents. Even if they are genuine, it may become necessary to decide their origin, if anonymous, whether they contain writing in recent ink, and the date of writing. Occasionally evidence of identity may be secured by the development of fingerprints upon paper. These are examples of factual demonstration which are not necessarily concerned with the genuineness of the document as such. Forged documents, of course, remain as the principal problem met with, but the term questioned document more completely defines the subject matter of this kind of enquiry.

The Materials.—Essentially the materials of a document examination of any kind are the paper and ink or pencil. There are, of course, documents produced with neither of these materials which may be in question. In practice, however, it is not of great importance to consider them. It is sufficient to assume for all practical purposes that the investigation will be concerned only with paper and ink or pencil.

All paper, which consists essentially of cellulose, and most inks can properly be described as chemical entities. Thus the materials are amenable to chemical examination which may and often does throw light upon their constitution. From the chemical state of the paper or ink, inferences important from a forensic point of view can often be drawn. This is particularly true of ink, first, because it varies greatly in composition, and secondly, by reason of chemical changes which take place in it as it matures on paper. Essentially, chemical examination, which is significant from a forensic point of view, consists in a study of the ink and the changes which it undergoes.

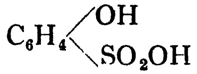
Pencil writing has also some forensic importance. Chemically, however, it is of less importance than ink on account of the stable nature of the material used for the manufacture of the pigment. Since in modern pencils this consists mainly of graphite with a suitable filler, it does not undergo the changes associated with ink.

The so-called indelible or copying ink pencil is more readily amenable to chemical examination since it contains aniline dyes of varying types. Chemical tests of a conclusive nature are thus often applicable.

Types of Ink.—There are many varieties of ink but all modern ink is essentially of five types: carbonaceous inks, iron gall inks, iron gall inks with provisional colouring matter, logwood, and aniline inks.

Carbonaceous inks are very ancient, and the modern type does not differ essentially from the original. It consists of finely divided purified carbon which is mixed with gum. It is now generally supplied in liquid form.

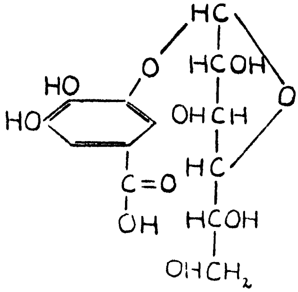
Iron gall inks are in the historical sense much more modern than carbonaceous inks. They were not greatly used in Europe until the sixteenth century. They consist essentially of gallates and tannates of iron. It is, however, important to note that whilst iron is generally necessary many other substances can replace tannin. Condensation products of formaldehyde and phenol and their esters produce inks with iron salts.

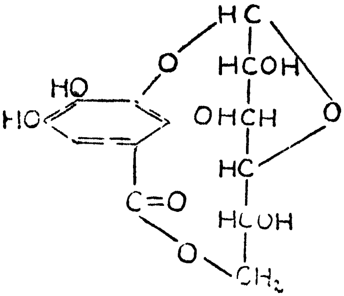
It has long been known that the intensity of colour depends upon the hydroxyl structure of the organic agent. Thus Schiff (*An. Chem. Pharm.* 1871, *clix*, 164) was apparently the first to observe that the colouration was proportional to the hydroxyl groups. Thus phenol sulphonic acid  $C_6H_4\begin{cases}OH\\SO_2OH\end{cases}$ gives a violet colour with ferric salts. Gallic acid 3:4:5 $C_6H_2(OH)_3$ COOH gives a more intense blue-black coloration.

In their classical *Eisengallustinten* Schluttig and Neumann asserted that permanent pigments of this type were produced only by compounds with three juxta-posed hydroxyl groups. Whilst haematoxylin, then believed to have the constitution $C_6H_2(OH)_3.C_6H_4.C_6H_2(OH)_3$ and gallic acid $C_6H_2(OH)_3$ COOH produced permanent coloration with iron salts hydroquinine $C_6H_4(OH)_2$ did not yield an ink.

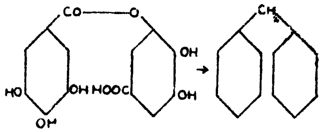
Mitchell (*Analyst*, 1903, *xxviii*, 146) has shown that Schluttig and Neumann's conclusions relating to hydroxyl groupings also hold good for inks prepared with ammonium vanadate in place of iron, vanadium compounds being also "ink forming" substances. In view of more recent studies of the constitution of haematoxylin these conclusions must be modified.

Constitution of Tannic Acid.—In regard to the constitution of tannic acid *Feist* (*Chem. Zeitg.*, 32, 1898, 918) isolated an acid and a lactone to which he attributed the following formulæ:





Nierenstein (*Ber. d. chem. Ges.*, 1905, 3641) obtained diphenylmethane by reduction of tannic acid and thus attributed the following formula to it:



By hydrolysis of tannic acid, Wittstein obtained gallic acid

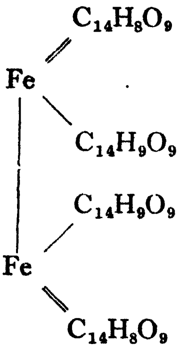
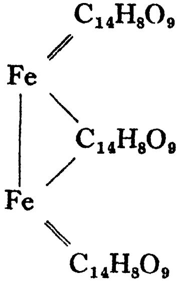
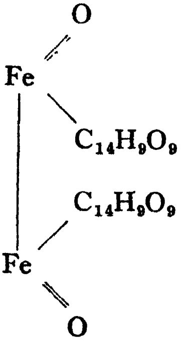
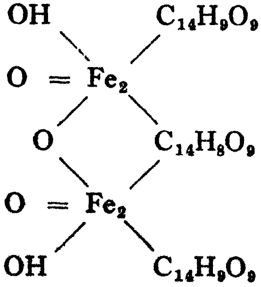
$$C_6H_2(OH)_3CO.OC_6H_2(OH)_2COOH + H_2O \longrightarrow 2C_6H_2(OH)_3COOH$$

Fischer also regarded tannic acid as galoylgallic acid.

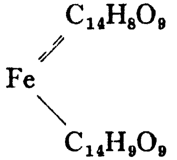
The structure of tannic acid cannot be said to be fully understood, but it seems probable that it contains three juxtaposed hydroxyl groups and that Feist's formula cannot therefore be accepted.

Tannates of Iron.—The manner in which the iron is combined in tannate of iron is not completely understood. The question, however, has considerable forensic importance because the changes which the iron salts undergo when ink is oxidized on paper have a bearing upon the age of the ink and thus upon the period at which the document was written. The table below represents the formulæ of various tannates of iron calculated by Schiff on the bases of Wittstein's findings:

Formula	%Fe_2O_3 calculated	%Fe_2O_3 found
$C_{14}H_9(FeO)O_9$	20, 3	10, 15
$C_{14}H_4(FeO)_3O_9$	44, 8	42, 8
$C_{14}H_6(FeO)_4O_9$	52, 8	42, 8–56, 3
$C_{14}H_5(FeO)_5O_9$	59, 0	56, 3
$Fe(C_{14}H_9O_9)_3$ $\vert$ $Fe(C_{14}H_9O_9)_3$	7, 6	8, 4

Formula	Fe_2O_3 calculated	Fe_2O_3 found
	11, 5	12, 0
	14, 9	13, 4 14, 9 15, 4
	20, 3	20, 15
	25, 2	25, 0

Whilst these formulæ are of great interest as indicating the existence of several different forms of iron tannate they throw very little light upon its actual constitution or upon the changes which take place when the compounds are oxidized. In this connection another author, Hindrichsen (*Die Untersuchung von Eisengallustinten*, 1909) attributes the following formula to ferric tannate formed on the paper by oxidation.

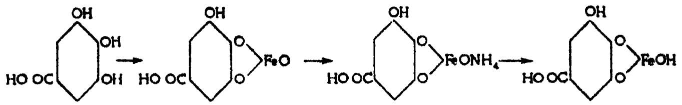


$$\mathrm{Fe}\begin{matrix} /\!\!/\, C_{14}H_8O_9 \\ \backslash\, C_{14}H_9O_9 \end{matrix}$$

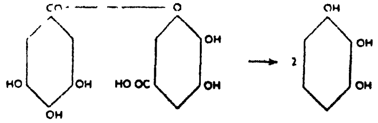
He does not, however, put forward any conclusive evidence in favour of this formula.

The whole question of the oxidation of ferrous tannates in ink is still very obscure. Wittstein's formulæ do not include ferrous salts at all, those which are not ferric salts being of a basic type. At the same time, it has been experimentally shown that fresh iron gall ink does contain ferrous iron. It has already been observed that the oxidation of ink upon paper has considerable importance in judging the age of an ink-written document, but it has to be admitted that the mechanism of the change of the salts from the ferrous to the ferric state is very incompletely understood.

Silbermann and Ozorovitz (*Chem. Zentr.* 1908, II, 1024) synthesised a compound from ferric chloride and gallic acid which on treatment with ammonium hydroxide and subsequent hydrolysis formed a derivative which they describe as hydroxy-ferrigallic acid.



More recently, however, Zetzsche (*Ann*, 1934, 435, 233; 1925, 445, 283) has studied the oxidation of ink. This author has found that on oxidation carbon dioxide is liberated. The conclusion is drawn that the compounds contain carboxyl groups. Zetzsche considers that the unoxidized ink consists of a soluble ferrous digallate and an insoluble ferrous monogallate and tannate. The preliminary pale colour of the ink is due to these compounds. On oxidation he considers that ferric monogallates and ferric pentatannates are produced. He appears, however, to consider that these salts are " acid " salts, that is to say that they include free carboxyl groups. They are blue-violet in colour. Esterification, however, takes place as the ink increases in age. These are described as secondary compounds. They have a brown tint and are probably ferric compounds of pyro-gallol.

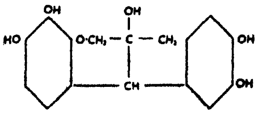


It is thus probable that Zetzsche's first product is, *inter alia*, hydroxyferrigallic acid, and the more complex oxidation products of polymerised hydroxyferrigälloylgallic acids with FeOH groups attached to pairs of hydroxyl groups in the ortho position.

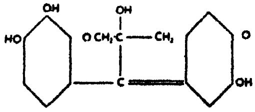
Metzger, Rall and Heess (*Zeitschr. fur angew. Chem.*, 31, 1931, 645 ; *Beitrage z. krim. Sympt. u. Techn.*, *Arch. f. Krim.*, 92, 1933, 107) have made elaborate examinations of the pH values of ink on paper. They find that the average pH of paper = 4 and the lowering of hydrogen ion concentration of ink on paper is explained by them as being due to the buffer effect of aluminium sulphate present in paper. They appear to conclude that the natural acidity of inks inhibits the formation of ferric salts. But the reduction of hydrogen ion concentration brought about by contact with the paper increases the rate of oxidation of the iron.

These investigations which are of some practical importance will receive further consideration. Whilst much of the work of these investigators is of a fundamental character, it has bgen applied in particular by Metzger, Rall and Heess to the study of criminalistic and related questions.

Constitution of Logwood Inks.—Logwood contains two well-defined compounds to which its pigmentation is due, haematoxylin and its oxidation product haematein. Rammstedt (*Tinte und Tuche. Chemischer Technologie der Neuzeit 2 Auf. V. Bd.*) accepts Perkin's constitution of haematoxylin and considers haematein to have the constitution shown below.



Haematoxylin



Haematein

It will be noted that the constitution does not include three adjacent hydroxyl groups so that its behaviour does not agree with Schluttig and Neumann's theory concerning the pigmentation of ink-forming compounds.

The nature of the reaction between haematoxylin and the metallic salts is probably different from that of metallic salts with tannic acid and gallic acid.

The property of pigmentation under these conditions has nevertheless caused it to be used for many years as a constituent of ink. Lewis in 1748 made use of logwood to increase the colouration of iron gall ink. Later Runge (1847) found that logwood, when heated with potassium chromate, produced a deep black solution which made satisfactory ink. It had the advantage of being neutral and thus did not corrode the pen.

Inks With Provisional Colouring Matter

Eisler in 1770 first introduced indigo into iron gall ink as a provisional colouring matter and to increase the intensity. Indigo was first used in this country in 1836. Unoxidized iron gall ink is very pale in colour. Indigo and later aniline dyes thus became common constituents of iron gall ink.

The reactions that take place between provisional colouring matters and iron gall ink are not understood but they are in some cases probably of a very complex character. The present author (*infra p.* 108) has shown that indigo retards if it does not entirely inhibit the oxidation of the ferrous iron in ink. This ink nevertheless attains great intensity of colour after it has been in contact with the paper for some time. It would thus appear either that the intensity of the coloration of ink does not essentially depend upon the oxidation of the iron or that the indigo reacts with the gallotannate of iron to produce a highly coloured compound more complex than the gallotannate.

Aniline dyes are also now largely used as provisional colouring matter in iron gall ink. They appear to exist in the ink essentially unchanged in the primary stages. Mitchell, however (*Documents and their Scientific Examination*) has made interesting observations concerning the changes in mature ink which contains provisional aniline colouring matter. After some years the aniline dye ceases to diffuse when treated with appropriate reagents. Mitchell suggests that this is due to the formation of a resinous tannate which mechanically fixes the dye. From the forensic point of view this property is very important since it gives an indication of the age of the ink (*infra p.* 93). The observed formation of a resinous tannate is also of interest. The resinous gallotannate probably corresponds with the ferric pentatannates of Zetzsche.

A wide range of aniline dyes are appropriate as provisional colouring agents, but in practice aniline blues are commonly used. The well-known blue-black effect is produced in this way. While the ink is fresh, aniline colour predominates but as the ink oxidizes it becomes darker. The colour appears black under the naked eye but dark purple microscopically. In some circumstances colour is an index of the age of the ink (*infra p.* 92).

Aniline Inks.—Coloured inks are commonly aqueous solutions of aniline dyes to which are added some stabilizing agent such as glycerine or gum. Red, black, green, violet and blue are the most common. Both basic and acid dyes are employed for their preparation. On the Continent a much wider range of colours is used as provisional colouring agents than in this country. In England the most common aniline ink is the black nigrosine fluid. These inks are particularly suitable for fountain pens. Their disadvantages are that the colour is fugitive so that they are unsuitable for documents in which permanency is required. Nigrosine ink does not fade but it can be easily removed from paper by washing.

Carbonaceous Inks.—These inks are less important from a forensic point of view today since they are less widely used. Chemically they are of less importance than other inks because they consist essentially only of purified and finely divided carbon suspended in a vehicle of water and gum. At the same time, carbonaceous inks are of great antiquity and were largely employed throughout the Middle Ages. Forensically disputes may arise concerning the authenticity of ancient documents which will require the examination of a carbonaceous ink. The simplicity of their composition and the fact that they remain practically unchanged with time makes their identification a fairly simple matter. Their chemical inertness precludes the more elaborate type of examination which may usefully be applied in the case of other inks.

(b) The Chemical Examination of Ink on Paper

General.—The examination of ink in the form of writing is essentially a problem of micro-chemical technique. This has been recognized for many years. The methods used today are, in fact, founded upon research effected by Robertson, Hoffmann and others in the late nineteenth century. The principle of their methods was to apply small quantities of reagents to ink strokes, and note the reaction which took place. The reagents commonly used were acids, alkalis, reducing and oxidizing agents, and reagents for the identification of individual constituents such as iron. Robertson and Hoffmann recommended the use of a gold nib or glass rod to carry out the tests, minute drops being applied to the ink strokes.

Developments of Chemical Technique. — These classical methods with suitable modifications are still in use today. They have been systematized and brought up to date by Mitchell (*Documents and Their Scientific Examination*). The types of reaction involved are that the acids react upon the iron tannate, the reducing agents, nascent hydrogen or chlorine have a bleaching effect. The oxidizing agents also produce bleaching of a less marked kind.

Bischoff (*Beiträge zur Kriminalistische Symptomatologie und Technik*) uses a similar technique in a somewhat elaborated form. He employs weak acids, strong acids, alkalis, oxidizing agents, reducing agents, reagents to identify iron, and special reagents.

These methods also involve the application of a different technique to the performance of the test itself. In the identification of iron, for example, the acid is applied to the ink stroke and the spot is then transferred to filter paper upon which the test is carried out. This may appear to be an unimportant modification, but in fact it represents a radical departure from the earlier method which consists merely in " spotting " the ink stroke and observing the reaction *in situ.*

Technique External to the Document.—The departure consists in the actual removal from the documents of the materials of which it is composed. From a practical point of view this modification is of great importance. It involves greater alteration to the document itself than the spotting method. This must be noted because in a criminal enquiry it is essential to alter the documents examined as little as possible so far as this requirement is compatible with efficiency in examination.

Method of Ward.—One of the least drastic of these methods is that advocated by Ward. (*Analyst*, 59, 1934, 621–2.) A capillary is used from which a small drop of the reagent is delivered inferior in diameter to the breadth of the ink stroke. The drop is protected by covering with a small watch glass, and the reagent is left in contact with the ink for about two minutes. The same capillary emptied of the reagent is then used to withdraw the reagent. The drop is then transferred to a microscopic slide and allowed to evaporate.

The preparation can then be treated with suitable reagents and the reaction observed under the microscope.

This method is of great practical value in many cases, and is probably capable of considerable development in practice. There is no other form of treatment which makes possible the actual transference of a given quantity of ink to an external medium. This fact has interesting implications from the point of view of quantitative micro-determinations. In the case of fresh inks which are water soluble, it should be possible to transfer a given quantity unchanged to the external medium. The case is different where mature inks are concerned which cannot so readily be removed by solvents which leave them chemically unchanged. This limits the application of the method in a direction which would make it extremely valuable if it could be applied in every case. At the same time this technique is a considerable advance upon classical methods of micro-chemical examination.

Methods of Metzger and Heess.—The methods of examination advocated by these workers, involve the actual removal of small portions of the document. Without this preliminary the tests cannot be carried out. Thus, whilst this technique is more fundamental than the more or less empirical tests of the classical type, it must be used with greater discretion, and in many cases it cannot be used at all. The chemical examiner must bear in mind the essential fact that the minimum damage must be done to the document examined. He will otherwise become involved in great difficulties when the case is tried. It is for this reason that the simpler classical tests are still largely used in practice.

Method of Carrel.—On the other hand, research has been carried out with a view to applying the methods of " decoupage " while at the same time doing the minimum of damage to the document. Carrel (*Contribution à l'identification des êncres en criminalistique Thèse de Lyon*, 1934) has devised interesting methods for this purpose. Essentially the method consists (1) in the actual transfer of a portion of the ink from the document to an external medium and (2) the transfer of the ink accompanied by a small portion of the cellulose substratum to an external medium. These are modifications of the methods advocated by Bischoff and Schneeberger who make an incision into the document with a small scalpel to remove the portions to be tested.

Carrel's method is (i) to apply a drop of collodion to the ink stroke to be tested. A microscopic slide is then placed on the spot, and heavy pressure applied. The collodion on drying forms a film which adheres to the slide and absorbs a portion of the ink. This method was finally abandoned in favour of (ii) by reason of the fact that not every kind of ink can be transferred in this way and that with some types of paper the collodion adhered too strongly. The present author has, however, found the method quite satisfactory in certain cases, if it is used with discretion.

Method (ii). The use of a gelatinized film is more generally adopted. The material used may be either photographic film which has not been sensitized or glass slips covered with a fine film of gelatin.

The transference is effected by slightly moistening the ink stroke with distilled water and then applying the gelatinized surface to the moist area with pressure. The slide or film is then lifted sharply. The ink stroke together with a portion of the cellulous substratum is thus transferred to the gelatin.

If carried out by a practised hand this method of transference does little more damage than the classical spotting methods. From the point of view of analytical technique, the analyst is left with a microscopic preparation which can be much more conveniently and completely examined than if the same area of the document itself were examined.

Comparison of the Methods.—The chemist called upon to make a chemical examination of a document must first decide what technique of examination he proposes to use. He must bear in mind that there are two objects which are not completely compatible in view. First, it is necessary to make as complete a chemical examination as possible and secondly, as little damage as possible must be done to the documents.

The special circumstances must decide which general method is to be followed. In many cases a certain amount of local damage provided it is not extensive is permissible. On the other hand documents of intrinsic value must obviously be treated with special care. It is, of course, true that no chemical examination can be made which does not involve some damage. Sometimes it is stated that by very skilful manipulation chemical tests can be performed the effects of which are not afterwards visible to the naked eye. It is not, however, the present author's experience that an efficient chemical test can be restricted to so small an area that no visible trace remains.

In general, methods which involve the actual removal of ink from its milieu entail more damage than treatment of the document direct. On the other hand the treatment of detached fragments eliminates the risk of accident which may involve extensive injury to the document. Clumsy manipulation of spot testing is a very dangerous proceeding, and those not experienced in its application should be very cautious in its use.

Certain tests to be described later cannot be performed upon the document direct without serious injury to it. When these tests are to be made no alternative presents itself.

Application of the Methods.—The spot testing of ink is best carried out by delivery of the reagents from fine-drawn capillary pipettes. Ordinary glass tubing can be used. The wide end can be fitted with a piece of rubber tubing closed at the other end with a piece of glass rod. The pipette can be fitted with a stopper which becomes

Table I

INDENTIFICATION OF INKS (Robertson and Hoffmann)

Ink	Oxalic Acid	Citric Acid	HCl 10%	H_2SO_4 15%	HNO_3 20%	$SnCl_2$ 1 HCl 1 Water 1	SO_2 Sat Sol.	$AuCl_3$ 4%	$Na_2S_2O_3$ 1 NH_4OH 1 Water 10	K_4FeCN_6 1 HCl 1 Water 10	NaOH 4%	Chloride of lime
Iron-Gall	Bleached	Bleached	Bleached yellow	Bleached	Bleached	Bleached	Bleached	Bleached slightly	Dark red	Blue	Dark red	Bleached
Logwood with K_2CrO_4	Violet	Violet	Red-purple	Red	Red	Red	Dull violet	Red-brown	Unaltered	Red	Brown	Bleached
Logwood with $CuSO_4$	Orange	Orange	Blood-red	Red-purple	Red-purple	Magenta	Red	Brown	Dark blue	Brick-red	Becomes dark red	Bleached
Nigrosin	Unaltered	Runs, becomes blue	Little alteration	Unaltered	Runs	Unaltered	Unaltered	Unaltered	Becomes dark violet	Unaltered	Becomes dark violet	Brown
Vanadium	Bleached	Bleached	Bleached	Bleached	Bleached	Bleached	Bleached	Unaltered	Runs	Unaltered	Becomes dirty brown	Unaltered
Resorcinol	Brill. red	Bleached	Brill. rose	Brill. red	Brill. rose	Bleached	Bleached	Becomes brown	Brown	Rose	Unaltered	Brown

the stopper of the reagent bottle. It is desirable that every reagent bottle be fitted with a pipette of this type.

A small drop of the reagent of any required size can be delivered from a pipette of this kind by gently squeezing the rubber tubing. This method is in our view, preferable to the use either of a glass rod drawn out to a point, or that of a pen, feather or other instrument. In our experience, in fact, both pens and feathers are very unsatisfactory for delivery of reagents.

In Table I, Robertson and Hoffmann's micro-chemical results are recorded. These tests are still of value for distinguishing between the inks described.

Table II (Lucas), is of value in distinguishing iron gall ink with provisional colouring matter, and Logwood ink.

Table II

IDENTIFICATION OF INKS

A. Lucas, *Forensic Chemistry*, p. 102

(Edward Arnold and Co., London, 1935)

Reagent	Iron Gall Ink without blue Colouring Matter	Iron Gall Ink with blue Colouring Matter	Logwood Ink
Hydrochloric Acid	Slightly yellow	Blue	Red
Oxalic Acid	Bleaches	Blue	Red
Tartaric Acid	Bleaches	Blue	Light brown
Acetic Acid	Bleaches	Blue	Violet
Sodium Hydroxide	Reddish-brown	Reddish-brown	Brown
Potassium Ferrocyanide	Blue	Blue	—
Potassium Thiocyanate	Red	Red	—
Sodium Hypochlorite	Bleaches	Bleaches	Bleaches

Poix, formerly of our Laboratory of Technical Police has devised a more elaborate scheme for the identification of different types of

Table III

IDENTIFICATION OF INKS

Coloured Inks (Poix)

Colouring Matter	Solution in Water	HCl	HNO_3	NH_4OH	$Al_2(SO_4)_3$ K_2SO_4	KCN	Chloride of Lime
Prussian Blue	Soluble with blue colouration with oxalic acid	Green colouration, then yellow solution	decolourized when warm	decolourized when warm	—	—	—
Cochineal	Solution in water, reddish-yellow	Orange	—	Violet	With NH_3 dark red	Dark red-purple	Decolourized white ppt.
Tannin	Feeble yellow	Greenish yellow	—	Dark yellow	—	Reddish	Blue-green decolourized
Indigo Carmine	Blue sol.	Lighter blue	—	Green when heated, light blue	—	Lighter, then light blue	Decolourized

aniline dyes and vegetable colouring matters commonly present in inks. (Tables III and IV.)

Bischoff (*supra*) recommends the use of the following reagents. 3% oxalic acid, 10% tartaric acid, hydrochloric acid from 10% to 0·1%, sulphuric acid 15%, nitric acid 20%, sodium hydroxide 4%, potassium hydroxide 4%, strong ammonium hydroxide solution, calcium hypochlorite, stannous chloride in hydrochloric acid 10%, sodium thiosulphate in ammonia, 10% potassium ferrocyanide, potassium thiocyanate, sulphurous acid and gold chloride.

Mitchell (*loc. cit.*) considers that in ordinary circumstances the following reagents are sufficient:—hydrochloric acid 5%, oxalic acid 5%, stannous chloride 10%, nascent hydrogen, HCl 50% with zinc. Saturated bromine water, sodium hypochlorite, 10%, titanous chloride, potassium ferrocyanide 5% in 1% HCl.

Interpretation of Results.—The method of interpreting the results of these tests is mainly empirical. They are not primarily designed to identify the constituents of the ink as such, but to compare the results of testing one ink with those of another. The inks tested are assumed to be of the same composition if the results agree and of different types if they do not. On the other hand the manner in which certain classes of ink behave to these reagents has been ascertained by experiment, so that the ink can be positively identified on the basis of these tests. Mitchell has stated, for example, that twenty-five types of commercial writing inks have been identified by the use of these reagents. It is essential, however, not to forget the limitations which are necessarily attached to empirical tests of this kind. They must be checked whenever possible against experiments with known types of ink. Two inks of the same composition, for example, may react differently to the same reagents if their physical and chemical condition due to age is different. In short, the results of the analysis must not be interpreted rashly. A fundamental distinction must be preserved between the test which positively identifies a given constituent and the empirical form of comparative test of which the mechanism is not understood.

Micro-Chemical Applications in Carrel's Method.—Where the ink stroke is transferred with its substratum as in Carrel's method a different technique is followed. In the first place the reaction can be observed under high magnification on the stage of the microscope. The preparation is mounted on a microscopic slide and protected with a cover slip. The examination should be made before any reagent is used. By this means the quality of the ink as distinct from its composition may be inferred. For example, ink containing dust can be identified in this way. Since ink transferred by this method is examined in thin

Table IV

ANILINE INKS (Poix)

Ink	Water	Alcohol	H_2SO_4	Dil H_2SO_4	HCl	NaOH or KOH
Malachite Green	Sol.	Sol.	Brownish-yellow	Dark green, dark yellow	Red-brown	In the cold dirty green ppt. Warm red
Brilliant Green	Sol. Blue green	Sol Green	Yellow-brown	Yellowish-green	Yellowish-green	Cold, green. Warm reddish
Fuchsine	Sol.	Sol	Reddish-yellow	Red	Reddish-yellow	Cold, reddish ppt.
Methyl Violet	V. sol.	V. sol	Yellow	Green, then violet	Yellow-brown	Red-brown ppt.
Crystal Violet	Sol.	Sol.	Yellow	Green, then blue	Yellow when dilute	Violet ppt.
Methyl Green	Sol. blue-green	Sol. blue-green	Yellow-brown	Green	Orange. Dilute green	Decolourized
Eosine	Red fluorescent	Red fluorescent	Yellow when warm	Yellow-brown ppt.	Yellow-brown ppt.	Deeper colour
Erythrosine	Cherry-red	Red fluorescent	Yellow	Red-brown ppt.	Red-brown ppt.	—
Methylene Blue	Blue	Blue	Green	Blue	Greenish-blue	Violet warm, then violet ppt.

longitudinal section the structure of the stroke is readily observed and the presence of insoluble foreign matter detected.

The micro-chemical tests can be carried out by running a drop of the appropriate reagent under the cover slip. It is then possible to watch the reaction under the microscope.

Comparative tests can be carried out in the same way. Two ink strokes can readily be transferred to the gelatinized medium in such a way that they lie side by side and close enough to each other to be viewed in the same field of the microscope. The appropriate tests can then be applied and a pair of reactions watched simultaneously. Micro-chemical tests carried out under these conditions can be much more efficiently observed than if the tests are made upon the document itself. On the other hand they require more elaborate manipulation and greater practice for their efficient performance.

Micro-Chemical Methods of Metzger, Rall and Heess.—As we have said the methods of these workers involve a more drastic interference with the document than those previously described. In order to effect this type of examination, they advocate removal of portions of the document with a scalpel. The tests for chlorides and sulphates in ink are also of an elaborate nature which necessitate the use of comparatively large portions of material. After the test is completed the portion removed is replaced *in situ* and secured by means of transparent adhesive paper. From a practical point of view this is a disadvantage since there are frequently legal objections to methods of this kind. From a technical point of view, however, this manner of attack is the most satisfactory. The document is treated as a component in a series of chemical reactions, and its destruction or damage is ignored if the facts are demonstrated to the satisfaction of the analyst.

(c) Other Micro-Chemical Methods

As has been indicated, the micro-chemical methods described are in general of an empirical character. There are, however, circumstances in which more specific tests are applicable. These can be applied to inks containing mineral constituents whereby they may be differentiated. The mineral composition of logwood inks is an example. Although logwood inks frequently have an iron base, they may contain potassium chromate or potassium dichromate, aluminium salts such as alums or aluminium sulphate and copper sulphate. It is obvious that if these can be identified valuable conclusion may be drawn concerning the character of the ink or inks upon a document.

Micro-Chemical Detection of Inorganic Constituents. — It is advisable to use Carrel's method (*supra*) for securing the sample of ink to be tested. The advantage is that a representative sample of the ink to be examined is assured when it is separated in this way. On the whole it also does less damage to the document because to ensure the solution of the inorganic constituents by any wet method an acid solution is generally necessary which must be in relatively prolonged contact with the ink stroke.

Detection of Chromium.—There is no satisfactory chemico-microscopical test which can be applied to the detection of chromates in logwood ink. The reaction with diphenyl-carbazide (sensitivity 0·25 gamma) provides a satisfactory micro reaction.

The sample is very gently ignited upon a piece of platinum foil or in a micro crucible. The ash is taken up with a very small drop of dilute sulphuric acid. This drop is then transferred to a platinum loop and very cautiously evaporated to dryness. The loop is dipped into fusion mixture to which has been added about 15% of sodium peroxide and the loop reheated just to the point of fusion of the mixture. The bead is taken up in a small drop of O, 1N H_2SO_4 upon a porcelain tile.

The diphenyl-carbazide reagent should not be added direct to the test drop but should be placed close to it. It should then be very cautiously mixed with the test drop by drawing a portion of the reagent into it and watching closely for the development of a magenta colour. Finally the two drops can be completely united and gently stirred.

Detection of Iron.—The most satisfactory test for iron in logwood inks is the classical reaction with ammonium thiocyanate. A sample of the ink removed in the same manner is ignited gently as in the test for chromium. The ash is treated with dilute nitric acid and evaporated to dryness on a spotting tile with a current of warm air. It is generally advisable to add the reagent direct to the dry residue, to let the mixture stand for half a minute, and then gently stir.

Detection of Aluminium.—Aluminium can best be detected with alizarin by the formation of the aluminium lake. The sample is taken and ignited as before, and the ash taken up in dilute sulphuric acid. The solution is evaporated to dryness and a small drop of water added. The drop is then spotted upon a piece of absorbent paper impregnated with the reagent. The paper is exposed to the vapour of ammonium hydroxide and dried. In the presence of aluminium a red colour is produced.

Iron is not generally present in logwood inks containing aluminium; but if it is present it interferes with the reaction and must be separated. In our experience the capillary method of separation on the paper itself is not very satisfactory if small traces of aluminium are present.

The procedure is the same as in the previous case to the stage where the evaporated residue is taken up with a small drop of water. A very small fragment of solid potassium ferrocyanide is then added to the drop and the mixture gently stirred as soon as the crystal is dissolved. Filtration is then carried out by the capillary method already described (*p.* 25). The filtered solution can then be spotted direct upon absorbent paper impregnated with the reagent, exposed to ammonia vapour and dried.

Detection of Copper.—α-Benzoin-oxime (Cupron) is a very delicate test for copper with a sensitivity of the order of 0·1 gamma. Owing to the fact that aluminium may be associated with copper sulphate in logwood inks, the test must be carried out in the presence of ammonium tartrate.

The preliminary procedure is as before, but the evaporated solution must be taken up not with water but with a small drop of a 5 % solution tartaric acid. The drop is then transferred to absorbent paper impregnated with the reagent and immediately exposed to ammonia vapour. On drying, a green colour indicates the presence of copper.

If it is suspected that any of the metals sought are present in the loading or colouring matter of the paper a blank must be carried out on the paper itself because the sample separated by Carrel's method includes portions of the paper. The same procedure applies as for the examination of the ink itself.

These methods are illustrative of a more fundamental method of attack by means of a technique external to the document and the application of formal micro-chemical processes to the analysis of ink. It has great value in the examination of logwood inks because circumstances can and do arise in which it may be necessary to determine whether two logwood inks associated with a document or documents contain the same or different inorganic bases. The comparative testing of logwood inks by means of the colour reaction of their pigments are not very satisfactory, but when it can be demonstrated by means of a fundamental analytical process that inorganic bases of like or unlike composition are present much more definite conclusions can be drawn.

(d) The Maturing of Ink

General.—One of the properties of ink is that it remains chemically active for long periods of time when exposed to the air, particularly when it is in thin layers as in the case of writing on paper. This fact has considerable forensic importance because the physical and chemical condition of the ink may provide evidence concerning the length of time it has been upon the paper, and give an indication of the age of the document.

We have already indicated that these changes are very incompletely understood, and until more precise information is available concerning the constitution of the compounds produced by the interaction of iron salts and gallotannic acid very little fundamental progress can be made. On the other hand the behaviour of ink as it matures on the paper has been extensively studied and certain facts of value have become available. Much of the work carried out, whilst it has been of an empirical nature, is of value practically.

Micro-chemical technique is of great assistance in this study since the manner in which certain reagents affect the ink at different periods often throws light upon its age even where the reactions involved are not understood.

In micro-chemical technique colorimetric determinations may be included, and it will be well to consider these in the first place.

The Colour of Ink.—It is an old-established fact that ink darkens with exposure to air. The explanation of this is that the gallotannates of iron deepen in colour with oxidation. Other reactions of a more complex type probably take place, but there is no question that oxidation is accompanied by darkening in colour.

Mitchell (*Documents and their Scientific Examination*) has made a close study of colour changes in inks. He found that if ink were applied to paper in a thin wash, maximum intensity of colour was reached in about a week. Thicker layers, as in writing, attain their maximum colour more slowly. If enclosed in a book, eighteen months may elapse before the process is complete.

For the purpose of recording colour, Osborn's comparison microscope is used and Lovibond's standard tintometer glasses. Mitchell's table (loc. cit., *p.* 63) indicates the colour changes against blue, red and yellow taking place in three types of ink from the first to the forty-third day. The results showed that maximum intensity of colour was reached in all cases over this period.

Solubility in Water and Acid.—Ink can be copied by damping its surface and applying to it a second piece of paper with pressure. The solubility of the pigment is, however, a function of the time. Fresh inks can be copied readily, but the property is lost when the ink is old. Still (1891), Habermann, Esternieder and Persifor Frazer studied this question. Still found that if water were used iron gall ink produced faint copies after four weeks, whilst Habermann and Esternieder obtained results after five and in exceptional cases after nineteen months.

Carré (*C.r. xxviii* 1213) made tests with dilute hydrochloric acid. He found that with this treatment inks produced good copies after eight or ten years and faint reproductions after twenty years.

The results of copying are not concordant. This is probably explained by the varying composition of the inks studied. The presence of aniline dye will increase solubility in water and thus the property of copying, and many subsidiary factors probably influence the result. Mitchell rightly says that it is only in exceptional cases that tests of this kind can give precise evidence of the age of the ink. In cases, however, in which it is required to distinguish between a document very recently written and one more than some months old, the test may be of value. Zetzsche has shown (loc. cit.) that the insolubility of the iron tannates increases with time.

Solubility of Provisional Pigment.—Mitchell (*Analyst*, 1920, *XIV*, 247), has shown that slow oxidation of the preliminary ferrous tannate takes place, and that finally, another tannate is formed which contains a higher percentage of iron. The oxidized compound is of a resinous character and is highly resistant to solution in water or dilute hydrochloric acid. This resinification influences not only the tannate itself but the provisional colouring matter of the ink which is mechanically protected from the action of solvents. Thus with fresh ink a rapid diffusion of the aniline pigment takes place after treatment with dilute acids. As the insoluble tannate forms this diffusion becomes less marked and finally disappears. It has been shown that the provisional colouring matter becomes completely insoluble after four to five years.

pH of Ink on Paper.—Metzger, Rall and Heess (loc. cit., *p.* 78) have recorded the hydrogen ion concentration value of ink on paper. These workers have made the interesting observation that the chlorides found in the ink exist not as salts but as free hydrochloric acid. They state that the ferrous gallotannates first formed contain 1 molecule of free acid for every molecule of the ferrous salt. The production of the ferric salts is according to the equation :

$$2Fe^{++} + O + 2H^{+} = 2Fe^{+++} + H_2O$$

They consider also that the pigmentation of the ink is due to the conversion of the gallic acid to ferrigallic acid.

It would thus appear that the free acid plays a part in the formation of the ferric salt which finally reacts with the gallic acid to produce ferrigallic acid. In isolation this reaction would result in an increase in hydrogen ion concentration. The presence, however, of buffers in the loading material of the paper modifies this effect. These interesting conclusions should be considered in conjunction with those of Ozorovitz (loc. cit., *p.* 77). See also Zetzsche (loc. cit., *p.* 77).

The Diffusion of Chlorides.—In the sphere of practice these authors have studied the diffusion of the chloride upon paper. They have shown that as the ink matures the chlorides diffuse so that in fresh inks the chloride " stain " is small in area and concentrated ; in older inks it diffuses. The test for chloride is carried out upon a portion of the document which has been excised. 10% solution of sodium nitrite is treated with a 1% solution of silver nitrate until a precipitate of silver nitrite is formed. This precipitate is redissolved in 10% nitric acid. The fragment of paper is moistened in the solution the colour of the ink being destroyed by the nitric acid. Chlorides if present are thus converted to silver chloride. After thorough washing the silver chloride is reduced with an alkaline solution of formalin. The place occupied by the ink stroke then shows a black stain the colour and area of which is referable to the age of the ink. (Türkel.)

Diffusion of Sulphates.—Sulphates also undergo diffusion. In the test for this acid radicle, a fragment of the paper is treated with a 4% solution of lead nitrate containing 4% of perchloric acid and a few drops of a solution of potassium permanganate. This treatment bleaches the ink and converts the sulphates to lead sulphate. The paper is then thoroughly washed with water saturated with lead sulphate to remove the excess of lead nitrate. The residual lead sulphate is then converted to lead sulphide by treatment with an alkaline solution of sodium sulphide. A black stain is produced.

These tests have a limited application in practice. First, they are not applicable to documents the paper of which contains appreciable quantities of chlorides and sulphates. Secondly, an interpretation of the diffusion of the stains in reference to the maturity of the ink cannot be made with precision. Thirdly, the tests cannot be carried out efficiently unless considerable damage is done to the document. This does not affect the interest and value of the tests themselves from an investigational point of view. Means may be devised in which they can be practically applied to documents the paper of which is free from chlorides and sulphates.

The Oxidation of Ferrous Iron in Ink.—Whilst the nature of the oxidation reactions of ink is not completely known, the fact that the ferrous iron is—with some exceptions—completely oxidized is fully established. The rate of this oxidation, if it can be determined, is clearly an indication of the age of the ink. The present author (*Rhodes l'Identification du Fer ferreux dans les Encres. Thèse de l'Institut de Criminalistique de Lyon*) has investigated this question.

The quantitative performance of tests of this kind has been greatly facilitated by the use of the organic " spot " reagents already described. For the identification of ferrous iron in ink the reagent *αα'* dipyridyl was used. (*See p.* 96.) The tests can be conveniently carried out by spotting on filter paper. If drops of ink, for example, are weighed on to filter paper and a drop of the reagent applied, a zone of colour sharply differentiated from the colour of the ink spreads on the paper beyond the circumference of the ink spot. It was found that the coloration produced was proportional to the ferrous iron present, so that the iron in small quantities of ink could be estimated against standards prepared in the same way.

A comparison of these results with those obtained by the gravimetric investigation of iron by classical methods showed an error of the order of 12%. The table below shows typical examples of the results.

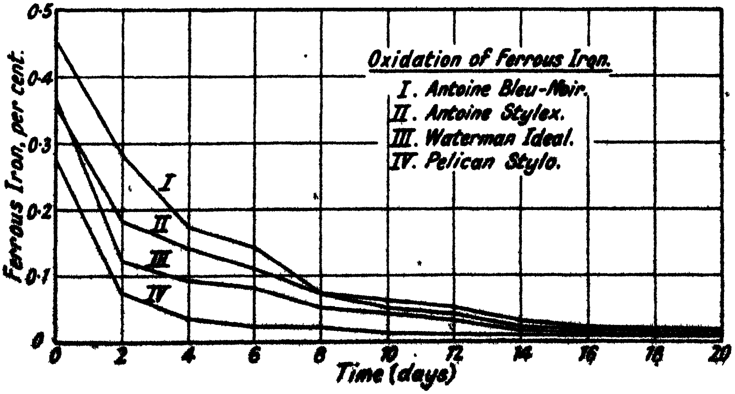
	Classical Method 10 gms. of ink Fe %	*Colorimetric Method* 5 mgms. of ink Fe %
Antoine Bleu-noir	0·40	0·45
Antoine Stylex	0·35	0·35
Waterman Jif	0·32	0·36

Thus while the method does not achieve a high order of accuracy, the colorimetric results being consistent among themselves make comparative studies possible.

Rate of Oxidation of Ferrous Iron.—Spots of ink exposed to air and light for regular periods of time showed progressive reduction in the quantity of ferrous iron present. The graph below represents the results obtained with four different types of ink. The ordinate represents the quantity of ferrous iron per cent, the abscissæ, the time.

The rate of oxidation is proportional to the quantity of ferrous iron present. At the same time, the period required to oxidize all but the last traces of ferrous iron was approximately the same (26–28 days), for all the inks examined.

Rate of Ferrous Oxidation in Ink Strokes.—It has not as yet been found possible to apply the quantitative method to portions of



ink upon the document itself. Qualitative tests, however, give results which are often of value. In the case of document examination a small drop of the reagent is applied to the ink stroke itself with a glass rod drawn out to a fine point. The reagent is left in contact with the ink for a minute, and is then recovered with a piece of filter paper. In prepared documents with different types of ink it was found that the iron was completely oxidized except for traces in 26 days to a month. Complete oxidation of the ferrous iron was never observed. Traces can always be detected.

Inks with Provisional Colouring Matter.—The presence of aniline dye as a provisional colouring agent does not appear to affect the oxidation of the ferrous iron. The so-called alizarin inks (those containing indigo) constitute an exception. Experiments with Stephen's ink containing indigo showed that inks which had been thirty years upon the paper still showed a marked ferrous iron reaction. This fact does not appear to have been previously observed. Some authors, in fact, have implied that the ferrous iron in inks containing indigo oxidize on paper in the same way as other inks. It has, however, long been known that the presence of indigo in liquid ink retards the oxidation of the iron. An oxidation-reduction state presumably accounts for this condition.

Reagents for the Test.—Hill (*Proc. Roy. Soc.*, 1930, 107 (*b*) 205), first suggested the use of $\alpha\alpha'$ dipyridyl as a reagent for the detection and estimation of ferrous iron. This author has observed that the sensitivity of the test is not affected between pH limits 3·5 and 8·5. The sensitivity is of the order of $0{\cdot}2\gamma$. F. Müller (*Mikrochem*, 1933, 12, 207) and others recommend the use of a 1 % solution in 0·1 N HCl.

We have found it necessary to increase the concentration of acid in the reagent since the complete solution of the iron is not effected with the concentration recommended. The reagent, therefore, consists of a 1 % solution of $\alpha\alpha'$ dipyridyl in 0·5 N. HCl. This reduces the sensitivity of the reaction to the order of 7γ. It is sufficient for the efficiency of the test in these conditions.

(e) The Chemical Examination of Pencil Writing

General.—Pencil writing is of two general types. (1) That produced with graphite pencil and (2) that of the so-called indelible pencil. Of these the indelible pencil is usually more amenable to chemical examination since the materials composing it are chemically more active. But it is not the case, as has sometimes been suggested, that a chemical examination of graphite pencil writing is of no use. Graphite pencils even of the best quality contain constituents which can be identified and which serve to distinguish one from another with some degree of precision.

At the same time pencil writing is not subject to the same type of chemical change as iron gall inks undergo on the paper. The writing remains more or less unchanged, and it is, of course, not possible to infer the age of pencil writing from a chemical examination of it. The scope of the examination of graphite pencil writing is necessarily much more restricted than that of ink whilst the examination of copying ink pencils more or less resembles that undertaken in the case of aniline inks. In spite of these restrictions definite conclusions can often be arrived at, if a suitable technique is followed in the chemical examination of pencil strokes.

PIGMENTS IN MODERN PENCILS

C. A. Mitchell. *Documents and their Scientific Examination.*

(Charles Griffin and Co., London, 1922.)

Pencil	Carbon	Loss at 210° C. Wax, Lamp-black	Ash	Silicates	Iron oxide and Alumina
	%	%	%	%	%
1. Acheson Graphite, No. 515, between BB and BBB	64·00	13·23	22·77	21·84	0·66
2. Conte, No. 5, about HH	57·19	8·41	55·53	36·29	5·35
3. Faber, hard pencil	50·60	5·26	37·55	32·42	1·99
4. Hardmuth's Koh-i-Noor, 2B	16·56	15·14	30·00	20·30	1·52
5. Hardmuth'sKoh-i-Noor, 6B	43·29	43·00	40·44	32·16	3·30
6. Japanese Pencil, HB	20·06	1·85	54·86	52·15	2·57
7. Rowney's Indelible	29·06	19·94	51·00	43·40	1·45
8. Spear. Carpenter's pencil	49·12	0·4	50·48	33·97	6·10
9. Wolff's Indelible	29·19	28·00	42·81	40·40	2·40

Composition of Graphite Pencils.—Graphite pencils are still commonly but incorrectly described as lead pencils. In fact, pencils containing lead practically disappeared at the end of the eighteenth century, although they are still in occasional use today for special purposes. Graphite has been used in pencils since the sixteenth century, but the use of anything approaching a pure composition is comparatively modern. High grade graphite was not unknown in the middle of the nineteenth century, but the composition varied between wide limits. Modern pencils are more standardized and those of good quality extremely constant in composition. The organic constituents are essentially carbon, lampblack and wax ; the inorganic ingredient is clay which is used as a binder. The table opposite shows the composition of well-known types of pencil.

It will thus be evident that the constituents are not such as to make an extensive chemical examination possible. There must be added, however, to the constituents chlorides, which are frequently present in graphite pencils, and sulphates are, according to Mitchell, occasionally found. Their presence, however, like that of titanium, is rare and they have therefore great value in identification of an individual pigment.

Qualitative Testing of Pencil Strokes.—The methods described for the examination of ink strokes (*supra pp.* 79–81) are also applicable to the examination of pencils. In testing the stroke for iron Mitchell recommends treatment of the writing respectively with a drop of acetic acid and a drop of strong nitric acid. Potassium ferrocyanide is then applied for the detection of iron.

Titanium is identified with hydrochloric acid and hydrogen peroxide. Chlorides when present are identified as silver chloride with silver nitrate, and sulphates with nitric acid and barium chloride.

A number of other empirical tests have been recommended which include the resistance of the pigment to strong acids, and it has also been suggested that the use of osmium tetroxide which is reduced by organic matter is a method by which the presence of wax can be detected in pencil writing.

Quantitative Analysis of Pencil Strokes.—The mere identification of constituents of this type is not generally of great value in the differentiation of pencil pigments. With the exception of titanium they are present in most pencils. For this reason Dennstedt, Voigländer, Türkel and others attach very little importance to a qualitative examination. Jacques Locard (*Thèse de Lyon. Analyse des traits de crayon*), has, however, elaborated a form of examination of great interest. In a comparative sense it can be said to be quantitative.

INDENTIFICATION OF PENCIL PIGMENTS (J. LOCARD.)

Pencils	No.	Potassium Ferrocyanide		Ammonium Thiocyanate		Hydrogen Peroxide		Silver Nitrate	
		10%	·05%	10%	·05%	12 vol.	0·12 vol	10%	·05%
Graphite Conte 1010	0	+	+	+	+	+	—	+	—
Graphite Conte 1010	1	+	+	+	+	—	—	+	+
Graphite Conte 1010	2	+	+	+	+	+	—	+	+
Graphite Conte 1010	3	+	+	+	+	+	—	+	+
Graphite Conte 1010	4	+	+	+	+	—	—	+	+
Graphite Conte 1010	5	+	+	+	—	+	+	+	+
Conte a Paris 1038	1	+	—	+	—	+	—	—	—
Conte a Paris 1038	2	+	—	+	—	+	—	—	—
Conte a Paris 1038	3	+	—	+	—	+	—	+	+
Bagnol et Farjon 104	2	+	—	+	—	—	—	+	—
Papeteries Generales Lyon	2	+	+	+	—	—	—	—	—
Graphite Français 1068	1	+	+	+	+	—	—	+	—
Graphite Français 1068	2	+	+	+	+	+	+	+	+
Franbel Paris 1290	2	+	—	+	—	+	+	—	—
Aw. Faber, Cedre	2	+	+	+	+	—	—	—	—
Aw. Faber, Castell, H.B.		+	+	+	+	+	—	+	—
L. & C. Hardmuth 110	2	+	—	+	—	—	—	—	—
L. & C. Hardmuth, Koh-i-Noor, H.B.		+	+	+	+	+	—	+	—
Caran d'Ache 778 stenodactyl		+	—	+	—	+	+	+	—
Venus, special drawing, B.B.	0	+	—	+	—	+	—	+	+
E. Wolff, Royal Sovereign, H.		+	—	+	—	+	—	+	—

The principle of Locard's method is to employ reagents of decreasing concentration so adjusted that the stronger will produce a reaction with a given pigment and the weaker will not. Thus a certain group of pencil pigment may produce a reaction for ferric iron with a 5% solution of ammonium thiocyanate whilst the same group produces a negative result with the same reagent at 0·5% concentration. On the other hand other pigments react positively and negatively with different concentrations. In practice the tests are carried out with a pair of reagents with concentrations corresponding to 10% and 0·05%. The table (*p.* 99) indicates the scheme of the reactions.

Locard has pointed out that this method does not make individual identification of a pencil pigment possible. It does, however, ensure a higher degree of differentiation than the qualitative method. In the case of iron, for example, two types of pigment can be distinguished with certainty, those which react with neither reagent and those which react with the weaker. In regard to titanium, three reactions have been observed. The metal reacts with 0·12 vol. hydrogen peroxide. It reacts only with 12 vol. hydrogen peroxide or titanium is absent. In regard to chlorides there are three possibilities. The chlorides react with 0·02 N silver nitrate. They react only with 0·1 N silver nitrate or chlorides are absent. Using these pairs of reagents there is thus a 1/18 chance of error. A much higher probability of differentiation than in the case of a simple qualitative examination is therefore attainable.

Composition of Indelible Pencils.—The examination of pencil marks of this type is more closely related to the examination of ink strokes than to those of graphite pencils. Copying ink pencil pigment consists essentially of kaolin, graphite and aniline dye compressed into rods. The dye used is generally methyl violet. The composition can often be partly inferred from the colour of the writing. Where a kaolin or alumina filler is used, the colour is brighter than if graphite is present. The kaolin filled pigments are also softer and mark the paper more readily.

Tests of Copying Ink Pencil Writing.—Differential results can often be obtained by treatment of the pencil stroke with a small drop of distilled water. The speed of diffusion of the pigment varies with different pencils. In some cases the diffusion may be extremely rapid whilst in others a period of five minutes or longer may elapse before spreading takes place. These differences are due to the nature of the filler, its particle size and degree of compression. The quality of the dye also influences the result.

Similar tests may also be applied using alcohol and ether as solvents. In the case of these reagents the diffusion is always more rapid and the zones of coloration as the solvent spreads may also be distinctive.

Ash of the Pigment.—Mitchell (*Documents and their Scientific Examination, p.* 123), in an interesting survey describes among other features of the analysis of copying ink pigments, the colours of the ash. These are varied, being red, white, buff, putty coloured and yellowish-grey. In those rare cases where it is permissible to excise a portion of the document the pigment may be burnt in a micro crucible. The colour of the ash of the pigment can then be observed. A putty coloured or red ash indicates the presence of iron in varying proportions. A yellowish-grey ash indicates traces of iron. Alumina produces a white ash.

Analysis of the Aniline Dye.—Spot reactions of the same type as are applied in the examination of aniline inks can be used in the identification of pencil writing. It is essential to note, however, that the quality of the paper on which the writing is made has an influence upon the reaction. Thus, sized papers and absorbent papers give somewhat different colour reactions for the same dyes.

Mitchell recommends the use of nitric and sulphuric and hydrochloric acids, stannous chloride, sodium nitrite with acetic acid and titanous chloride. At Lyon we have been accustomed to use besides the strong acids, oxalic acid, sodium hypochlorite and potassium hydroxide.

Whilst they are of an empirical type these tests, particularly when used comparatively, give precise results. Mitchell reports an interesting case (*Rex v. Wood*), in which it was sought to identify an indelible ink pencil found on the accused with the writing upon a note which was found half charred on the scene of the crime. The reactions of the pigment of the pencil were compared with those of six others from which it was readily distinguished. The comparative tests applied to the writing of the pencil found and that of the note showed close correspondence. Identity of the writings was assumed, and was, in fact, later independently established.

(f) The Chemical Examination of Paper

The best quality paper consists of almost pure cellulose. Inferior qualities contain pecto-cellulose, ligno-cellulose and other impurities. Very inferior types contain fragments of undigested wood.

Besides the grosser forms of impurity paper may contain traces of substances used in its manufacture. In the sulphite digestion process the wood is treated with calcium bi-sulphite which removes the non-cellulose portions of the wood. Traces and in some cases appreciable quantities of sulphates are therefore not infrequently found.

Chlorides are also a common impurity. Their presence is due to the chlorination process to which the raw material may be subjected.

Other constituents are found in paper which are not impurities but loading materials to fill the pores of the paper. These materials include china clay, talc, chalk, and calcium sulphate.

Other additions are sometimes made for the purpose of colouring paper. These colouring matters are of two kinds, mineral and aniline dyes. Mineral pigments include ultramarine, prussian blue, lead chromate, oxides of iron and manganese. Among the aniline dyes methylene blue, auramine and metanil yellow are used.

The surface of paper may be sized with gelatin, glue, rosin, casein or starch. This treatment is adopted to give the paper a smooth or glossy surface.

Thus it is obvious that paper is a complex mixture which is highly characteristic chemically. A chemical examination will often give valuable evidence of identification.

THE IDENTIFICATION OF CELLULOSE FIBRES

Herzberg (*Papierprüfung*, 1915, *p.* 94.)

		Iodine and Pot. Iodide	Zinc Chloride and Iodine
I. Lignified Fibres	Mechanical Wood Pulp Jute Fibres containing undissociated cellulose	Fibres yellow to yellowish-brown according to lignification	Pale to dark yellow
II. Cellulose	Straw Cellulose Jute Cellulose	Grey	Blue to bluish-violet
	Wood Cellulose Andansonia	Grey to brown	Blue to reddish-violet
	Esparto		Blue to bluish-red
	Manila hemp	Some grey, some brown. Grey-brown and yellowish-brown	Blue, bluish-violet red-violet, dirty yellow
III.	Linen Hemp Cotton	Pale to dark brown	Pale to dark bluish-red

The Identification of Cellulose Fibres.—Herzberg (*Papierprüfung*, 1915, *p.* 94) recommends the use of two reagents, namely 1·15 gm. of iodine dissolved in 2 gm. of potassium iodide, 2 cc. of glycerine and 20 cc. of water, and (A) 20 gms. of anhydrous zinc chloride in 10 cc. of water and (B) 0·1 gm. of iodine dissolved in 2·1 gms. of potassium iodide in 5 cc. of water. Solutions A and B are mixed and the supernatant liquor decanted off.

Jenke utilizes a saturated solution of magnesium chloride with 23 gms. of potassium iodide and 1·5 gm. of iodine in 20 cc. of water. With this reagent, cotton, linen and jute cellulose give a blue coloration. Straw gives blue-violet, mechanical wood gives a yellow colour, chemical wood fibres are uncoloured or give a faint red.

Identification of Sizing.—**Gelatin.**—The paper is extracted with boiling water and the extract evaporated to a small bulk. The solution is treated with gallotannic acid. A flocculent yellow precipitate forms if gelatin is present.

Rosin.—For the detection of rosin the paper must be extracted with hot alcohol. The alcoholic solution is then treated with sulphuric acid and acetic anhydride (Storch-Morawski reaction). A red-violet coloration indicates rosin.

Casein. — If gelatin is absent, Millon's reagent for the detection of proteins is applied. Casein gives a pink coloration with this reagent.

In cases where it is necessary to isolate the casein, the paper is boiled with sodium carbonate solution. Acetic acid is added to the filtrate. The casein is precipitated and can be examined after washing free from the acid.

Starch.—Starch can be identified by the usual test with iodine.

Identification of Loading Materials.—The principal bases to be sought are aluminium (hydrated aluminium silicate), calcium (calcium sulphate), barium (barium sulphate), magnesium (magnesium silicate). If one of these bases is identified, it is an indication of the type of loading used in the paper. The " spot " reactions already described should be used. A small portion of the paper should be burnt in a micro crucible and the ash taken up with hydrochloric acid and evaporated to dryness. The alizarin test should be used for aluminium. Calcium may be detected with picrolonic acid. Diphenyl carbazide is used for magnesium.

Barium sulphate which is to a large extent insoluble in strong acids will remain as a white precipitate.

If one of these bases is present it will most probably correspond to one of the substances specified in brackets above. If aluminium and calcium are associated and sulphates are also present the loading material is probably a mixture of alumina and precipitated calcium sulphate, the so-called satin-white.

Identification of Pigments.—Pigments as we have indicated are of two kinds, inorganic and organic.

Blue.—Inorganic.) Blue papers of good quality are generally coloured with ultramarine, a double silicate of aluminium and sodium containing sulphur. Prussian blue, ferric ferro-cyanide or ferric potassium ferrocyanide of which several varieties exist is also used as a pigment.

Two simple tests can be applied for identification. Ultramarine is bleached by strong acids whilst Prussian blue is decolorized by alkalis.

A third blue pigment occasionally used in expensive paper is smalt (cobalt silicate). This has considerable interest since it has been little used in paper manufacture since the middle of the nineteenth century. Thus its presence may in some circumstances indicate the date of the paper. Smalt is readily detected because the ash of the paper containing it is blue. A confirmatory test for cobalt can be made.

Yellow.--Yellow papers may contain lead chromate. Chrome yellow and ferric oxide may be mixed to produce buff shades.

Brown and Green.—These papers may contain iron or manganese or a mixture of chrome yellow and Prussian blue. Appropriate tests for lead, iron and manganese require no special description.

Organic Pigments.—Organic pigments are readily extracted from paper by treatment with hot alcohol. It is generally sufficient to note the colour of the alcoholic extract and to apply the tests with acids and alkalis already described (*p.* 88).

THE APPLICATION OF MICRO-CHEMICAL METHODS TO THE EXAMINATION OF PAPER

Since it is generally necessary to examine micro quantities of paper so as to avoid obvious alteration of the document the methods described in the preceding paragraphs must often be adapted on a micro-scale.

Identification of Cellulose.—Herzberg's reagent containing iodine, potassium iodide and glycerine can be adapted on a micro-scale. A small portion of the fibre is stained with this reagent for one or two minutes on a microscopic slide. Excess of the reagent is then removed with filter paper, care being taken that none of the fibres of the paper becomes detached and mixed with the sample. A cover slip is then applied and the fibre examined under a low power. Linen, hemp and cotton give a brown coloration. Straw, jute, wood, Andansonia, Esparto and Manila cellulose give grey or grey-brown. Lignified fibres of mechanical wood jute and undissociated cellulose give yellow or yellow brown.

This classical test has been modified by Vetillard. The stained fibres from which the excess of iodine has been removed are treated with sulphuric acid of about 50%. The excess is removed and the preparation examined as before. Linen, Hemp and Cotton give violet. Cellulose gives blue. Lignified fibres give yellow. These colour reactions are sharper than those obtained with the iodine reagent alone.

Identification of Sizing.—The reactions described for gelatin, rosin, casein and starch are not readily adapted on a micro-scale. If, however, the reactions are observed under a low power with reflected light they may be perceptible. The Storch-Morawski reaction for rosin is, for example, fairly delicate. The reaction for casein is also fairly satisfactory for small quantities.

In regard to starch, it must be borne in mind that materials other than starch give a blue reaction with iodine. At the same time if a pronounced blue coloration is produced with a very dilute solution of iodine in potassium iodide, it is generally safe to assume that starch has been identified.

Identification of Loading Materials and Mineral Reagents.—Since this examination involves the detection of inorganic bases, the same general procedure is applicable as in the examination of micro-quantities of dust. In regard to loading materials, however, it is important to note that they may consist of metallic silicates. Fusion of the material may thus be necessary. This can be carried out on a platinum loop or on foil.

It should also be noted that it is a matter of some difficulty positively to identify small quantities of barium sulphate.

If barium sulphate is suspected the material should be fused with sodium carbonate. The mass is taken up in hydrochloric acid and the solution evaporated to dryness. It is taken up with a small drop of water spotted on absorbent paper and tested with rhodizonic acid.

For the reason already given the identification of the mineral pigment requires no special discussion. It should, however, be emphasized that before the chemical examination is made the colour of the ash should be very carefully noted with the assistance if necessary of the microscope. The colour of the ash may give a precise clue as to the nature of the mineral pigment. On the other hand if the ignited paper is coloured and the ash white organic pigments are probably present.

Interpretation of Results.—Since in a given paper it may be possible to identify (1) The nature of the cellular fibre. (2) The impurities. (3) The nature of the loading materials. (4) The sizing. (5) The colouring matter, very precise conclusions concerning the paper may be made available by a chemical examination. All these substances do not, of course, exist together in all writing papers, but the nature of the fibre can always be examined and the impurities sought. Loading materials are also generally shown. The object of the examination is either to match the paper with that of some other document, to determine the approximate date at which the paper was produced or to determine its origin.

Fraudulent Characteristics.—The watermark upon paper may have an important bearing upon its genuineness. The watermark is normally produced by means of a wire design fixed to the dandy roll so that the increased pressure at that point upon the pulp compresses it, making the surface more transparent.

Fraudulent watermarks are sometimes produced by the use of carnauba wax, spermaceti and a drying oil. If the paper is treated with ether the wax is dissolved and the watermark disappears.

Paper is occasionally stained artificially to give it the appearance of age. Various colouring matters of which an infusion of tea is one are used for this purpose. This type of fraud can usually be detected by inspection. Chemical tests can occasionally be applied, but no general rule can be laid down.

(g) The Examination of the Forged Document

General.—These are two types of forgery of documents: the imitative and the manipulative. Chemical examination is usually applicable only to the second type. Imitative forgery is confined to the imitation of a piece of handwriting. The detection of the fraud can generally only be achieved by physical examination with the microscope and by methods of micro-measurement. Manipulative forgery, however, involves the physical or chemical examination of the document. Alteration of this kind can often be detected by chemical methods.

Manipulative forgery is of two kinds (1) by addition to the document and (2) by subtraction from it. An example of the first form of technique is the alteration of figures or the interpolation of a word or words which alters the document's meaning. The second form of manipulation involves the removal of words or figures by chemical or physical means with the same intention.

The two forms of manipulation can, of course, be associated with the same document as when writing or figures are removed and others substituted. Again addition may involve the process of subtraction as when writing is scored out with a view to falsification.

An examination which aims at the detection of forgery of this kind may involve the examination of both the ink and the paper. In regard to the ink it may be required to decide (1) if the ink is of the same type throughout the document, (2) if the age of the ink is the same at all points, (3) if traces of the constituents of the ink remain the pigment having been removed by bleaching, (4) if the type of ink used is consistent with the reputed date of the document, (5) if the writing has been bleached out whether the text can be reconstituted, (6) if the ink is mixed with foreign material as when pencil writing has been inked over.

In regard to the paper, it may be necessary to determine (1) the type of paper used, (2) any manipulation of the paper, such as the fabrication of a watermark, the treatment of the paper with chemicals or mechanical interference.

Forgery by Addition.—Forgery by addition may be so clumsy as hardly to call for expert examination, or so skilful as to make it extremely difficult to detect even by the most refined methods. A common form of addition is the " raising " of cheques to a higher figure than that for which they were originally drawn, and the alteration of dates upon documents. In examples of this kind the alteration may only involve the change of a single figure and the addition of one letter to a word. Great care may be taken in matching the ink, and using a suitable pen to make the interpolation appear natural.

Forgery by Subtraction.—This method of falsification is more varied and elaborate. There are two general methods of subtraction, the physical and the chemical. The physical method which is the cruder of the two involves the removal of ink or pencil writing by erasure. It may be very skilfully performed so that there is little trace showing the point of attack. The surface of the paper may be restored by appropriate treatment.

The chemical method of deletion is usually known as " washing." Washing involves treatment of the document with a bleaching agent which decolorizes the pigment of the ink. If skill and knowledge are brought to this technique little evidence of the treatment remains. Acids such as nitric and oxalic acid are used for this purpose and bleaching agents such as sodium hypochlorite.

Chemical Examination.—It is first essential to bear in mind that the chemical examination of a document should not be undertaken if other methods which do not involve it can achieve the desired result. Photography both with ordinary light and with ultra-violet rays and infra-red sensitive plates has been greatly developed of recent years. A discussion of these methods would be out of place here. The fact is mentioned so as to emphasize the desirability of using these methods if they are applicable. In any case, before any chemical examination of a document is made, it must be photographed in natural size. In no circumstances must this precaution be neglected. It is also advisable to repeat that when a chemical examination is undertaken, the minimum damage must be done to the document. Every step should be carefully considered before it is undertaken. As far as possible the tests should be carried out in the least conspicuous parts of the document. When the experiments are not being done, documents must be protected between sheets of glass or cellophane.

The Chemical Examination of Erasure.—The simplest test should be made first. The most obvious is to hold the document up to the light to ascertain if more light is transmitted at the suspected point of attack. This simple test may be conclusive. In many cases, however, sufficient skill has been used to make the test uncertain. This is true in particular if the surface of the paper has been reconditioned.

Where the surface has not been reconditioned the paper may be exposed to iodine vapour. The result of this treatment is that the iodine is absorbed in the locality of the attack, and the manipulated area is thus clearly defined.

It is, however, preferable to use a volatile solvent such as benzene. If a drop is applied to the normal surface, it retains a circular shape. If, however, the paper has been manipulated by erasure, the benzene drop follows the contour of the point of attack.

If the surface has been reconditioned the suspected part should be treated with (1) water and (2) with alcohol. A piece of filter paper is moistened and applied to the paper, the process being repeated several times. If the reconditioning agent is water soluble, the erasure will be disclosed either by inspection or by one of the methods described. Treatment with alcohol will remove such substances as rosin.

Chemical Washing.—Various reagents are used for "washing" documents.

(1) Chlorine water.
(2) Sodium hypochlorite.
(3) Oxalic acid.
(4) Citric acid.
(5) Sodium bisulphite.
(6) A mixture of ammonium carbonate and sulphur.
(7) Potassium permanganate.
(8) Chromic acid in sulphuric acid.
(9) Solution of (i) potassium permanganate.
    " (ii) sodium bisulphite.

In regard to (6) the mixture is used dry in a small muslin bag which is rubbed gently over the ink to be removed. The result is not generally satisfactory. For certain kinds of ink, citric acid is a powerful decolorizing agent. (9) however, which in France is called a " corrector " and is used for non-criminal purposes, is very efficient. The potassium permanganate solution is first applied. This is then decolorized with the solution of sodium bisulphite. The processes are repeated until the ink is entirely bleached.

Mitchell has experimented with the bleaching effect of hydrochloric and oxalic acids and bromine water. All these reagents have a marked bleaching effect upon iron gall ink and those of the logwood type. Vanadium inks are most resistant to the action of bleaching agents.

Examination of the Washed Document.—Chevallier whose classical methods still have much to recommend them makes use of litmus paper to test the reaction of the suspected portion of the document. The application of moist litmus paper must, however, be used with caution if other tests are to be made.

It is preferable to make use of a more sensitive reagent such as the universal indicator. A minute drop of the indicator is applied to the suspected area. This is then removed with a piece of filter paper. A similar test is made upon a portion of the document which is known to be in its original condition. Any difference in the hydrogen ion concentration is noted.

Nature of the Bleaching Agent.—It is not generally possible to decide positively the nature of the bleaching agent used. It is advisable, however, to make a test for chlorides and for sulphates. A small drop of dilute potassium permanganate can also be applied. Decolorization will indicate that sulphites have been used for bleaching. These tests, however, must be used with discretion. They are not sufficiently conclusive to warrant the risk of defacing the document. It is in all cases advisable before applying any chemical test to examine the surface carefully with a lens and to note any local discoloration or other sign that the surface has been treated chemically.

The Reconstitution of the Text.—Chemical methods for the restitution of " washed " writing are often effective if the manipulation is skilful. The greatest care, however, must be taken or the document may be damaged and the desired result not achieved.

When ink writing is bleached the pigment only is removed. The iron salts although a portion of them may be removed remain upon the fibres of the paper. Classical methods for reconstituting a faded text included the use of gallic acid. A " true " ink is thus produced by reaction between the gallic acid and the residual iron. The method is not satisfactory and is now never used.

Potassium ferrocyanide is a more efficient reagent. The method of application is to soak a piece of filter or blotting paper with the reagent, place it in contact with the document and apply pressure in a copy press. In the case of newly washed documents, the method rarely fails to restore the writing. Much longer application is necessary in the case of older documents.

Before resort is had to the treatment with potassium ferrocyanide, it is necessary to ensure that the residual iron is in a soluble condition. It is thus advisable preliminarily to treat the surface with dilute nitric acid which is removed with water before the reagent is applied.

The most satisfactory method of development is, however, to treat the document with ammonium sulphide. The reagent must not be applied to the document direct, but in vaporized form. A satisfactory method of effecting this is to connect the Kipp apparatus with a wash-bottle containing ammonia. The outlet tube of the wash-bottle should be fitted with a funnel of convenient size. The document is rested upon the mouth of the funnel and arranged so that the suspected print is in contact with the vapours.

The time required for redevelopment of the text will depend upon the particular conditions. If the ink has been recently bleached the colouration may be restored fairly rapidly. Older documents react more slowly. The nature of the bleaching agent also affects the result. In general, acids act more drastically and remove a greater proportion of the iron, so that a text which has been acid washed is more difficult to reconstitute. The original iron content of the ink also, of course, influences the reaction. At the same time where an iron gall ink has been used, it is nearly always possible to reconstitute the bleached pigment by this method.

The reaction, however, is slower than that obtained with potassium ferrocyanide. If after four hours' treatment no result is obtained, the experiment can be regarded as negative, but it should never be abandoned at too early a stage.

Deletion by Scoring out.—Examples of this are rare in criminal cases, but they may occur in documents where it has been sought to alter the meaning by striking out a word or passage with ink. Such an act, equally with that of bleaching or erasure, may be forgery.

The greatest discretion must be used in employing chemical methods for the removal of the superimposed layer of ink. Resort should not be had to them until photographic methods with infra red plates or fluorescent photography have been tried and have failed.

First, micro-chemical tests should be carried out to decide if the two inks are of different composition and react differently to bleaching agents. If this is found to be the case the reagent chosen should be one which produces the maximum bleaching effect in respect of the superimposed layer of ink but where the effect is less marked upon the original ink of the text. Filter paper moistened with the chosen reagent is then applied to the deleted passage. The paper must be lifted from time to time to watch the progress of the bleaching and to ensure that it is not overdone. A piece of filter paper moistened with distilled water is then applied to remove the excess of the reagent. The present author (*Rhodes, The Scientific Examination of an Historic Document, Chem. and Industry, April 10th.* 1931, 303) has described in detail the method to be applied in a case where the ink of the text proved to be more resistant to bleaching agents than the superimposed layer.

In cases where a water soluble aniline ink has been deleted with an ink of an insoluble character, the author has made use of a copying method which is often successful. A piece of thick blotting paper is moistened with water and applied to the deleted passage. The blotting paper is covered with waxed paper and the whole is placed in a press for about half an hour. On removal of the blotting paper, the underlying writing is reproduced upon it, of course in reverse. The writing can then be read in a mirror. If the copy is very faint and cannot be read, it can often be made visible by examination under ultra-violet rays. This method is particularly successful in the case of red inks containing eosin. Even when only faint traces are visible by ordinary inspection, the passage may become completely visible under ultra-violet light.

In cases where the inks are of the same type, it may be impossible to bleach the superimposed layer without decolorization of the underlying ink. This, however, is not necessarily the case. If the ink used to make the deletion is of more recent date than that of the original writing, a suitable bleaching agent may remove the superimposed pigment, leaving the underlying text relatively unattacked.

Reconstitution of Erased Text.—It is not generally possible to reconstitute an erased text by chemical methods. But in exceptional cases this can be done. It has been shown that a proportion of the iron salts sink deeply into the fibres of the paper and thus cannot be entirely removed by erasure. In some cases the quantity is sufficient to make chemical reconstruction possible. Fuming with ammonium sulphide is, in our experience, the only method by which an erased text can be restored. The method described (*vide supra, p.* 110) should be used and the treatment should be continued for four hours. If the surface remains unchanged after this lapse of time, the experiment must be considered negative, but even if traces of iron sulphide are observed, the treatment should be continued for a further hour. In our experience the results even if positive seldom make the text legible, but the experiment should always be tried since reconstitution of the text can be effected by this means in exceptional cases.

Forgery by Interpolation.—Chemical examination of suspected interpolations involves the micro-chemical examination of the ink. Where words or figures have been altered chemical tests of the kind already described are applied, both to the genuine and suspected parts of the writing. A colorimetric examination should first be made with a comparison microscope. It must be noted, however, that differences in colour, even if pronounced, are not necessarily evidence of manipulation. The quantity of ink with which the pen was charged, and the local condition of the paper will influence the colour of the same ink.

Well-chosen micro-chemical tests will, however, generally distinguish between different types of ink. Whilst evidence that a document has been written with more than one type of ink is not proof of forgery, it is always a highly suspicious circumstance.

The increasing use of the fountain pen, and the consequent standardization of ink has tended to reduce the scope of tests of this kind. An insignificant interpolation such as the addition of a cipher after another figure made with the same ink as that with which the document was originally written presents great difficulties to the examiner. If it can be shown in cases of this kind that the suspected interpolation was made at a later date than the rest of the document there is then strong presumptive evidence of fraudulent manipulation.

An examination of the degree of oxidation of the ferrous iron in the ink may be of value in these circumstances (*see p.* 95). The present author has dealt with a case of a receipt in connection with which it was alleged that the actual author of the receipt had secured possession of it a fortnight after it was drawn for the purpose of altering the date. It was shown that the degree of oxidation of the ferrous iron in the ink of the suspected interpolation was less than in the ink of the undisputed parts of the document. The ink was, however, of the same type. This fact was consistent with the view that interpolation had, in fact, taken place at a later date.

THE DATE OF THE DOCUMENT

The question of the date at which a document was or was not written is one which is continually arising in connection with disputed documents. It may provide conclusive evidence of forgery or on the other hand establish the genuineness of a document, the authenticity of which is disputed. A chemical examination of the ink may in some cases supply the evidence required concerning the period at which the document was written.

There are certain historical facts which are relevant in this connection. Patents for the use of aniline dyes in ink were first taken out in England in 1861. The first aniline ink appears to have been made from Hoffmann's violet which was discovered in 1863. Eosine was discovered in 1874, and malachite green in 1878. It is thus obvious that if the presence of these pigments can be demonstrated in documents purporting to belong to a date prior to the discovery or use of these pigments, they are not genuine. Cavalho (*Crime in Ink*, *N.Y.*, 1929) describes a case in which he showed that certain marginal references in red ink in a document stated to have been written prior to 1874 had been made with a red ink containing eosine.

Method of Examination.—Fully matured ink retains its provisional colouring matter tenaciously (*see p.* 93). In order to bring it into solution it is necessary to treat it with concentrated acid. The ink stroke should be attacked with a drop of hydrochloric acid of a concentration of about 50%. After two or three minutes it is removed with a piece of filter paper. The spot is then neutralized with ammonium hydroxide. Aniline dye if present will then regain its colour. Appropriate tests can then be applied (*p.* 102) to identify it.

The combination of the provisional pigment with the iron tannate in mature ink has been studied by Mitchell (loc. cit., *p.* 93). The results in relation to the date of the document have wide application in practice. Mitchell recommends the use of a 5% solution of oxalic acid. The effect of this reagent upon fresh ink is to bleach the black pigment and liberate the aniline dye which spreads on the paper. With increasing age the dye diffuses less and less rapidly and after five to six years diffusion ceases altogether.

Whilst this test gives no indication of the precise date of the writing, it can distinguish fresh ink from that which is some years old with certainty. Thus in the case of Rex *v.* Pilcher, a disputed will was alleged to have been written in 1898. It was shown that the ink used to write a number of contemporary documents contained provisional colouring matter which showed no diffusion on treatment with 5% oxalic acid. Similar treatment of the ink on the will produced rapid diffusion of the aniline dye. It was thus concluded that the ink was less than six years old.

Locard (*Traité de Criminalistique*, *VI*, 793) uses a 20% solution of oxalic acid or a dilute solution of hydrochloric acid.

Copying Power.—Theoretically the solubility of the pigment in water and other solvents is an indication of the age of the ink. In practice, however, this method should not be applied except in special circumstances since it involves too large an area of the document. At the same time, if a copy can be made of an iron gall ink with water it is evidence that the ink is fresh. The method cannot be used to distinguish between inks which are close together in date, and it is not reliable except to distinguish fully matured ink from that quite recently used.

Chloride Diffusion.—Türkel developing the method of Metzger, Rall, and Heess for the detection of chloride (*p.* 93–94) has claimed that the area and depth of the stain produced on the paper by the reduced silver chloride makes possible an accurate estimation of the age of the ink on the document. In the present author's experience the technique is too complicated to recommend the method for general use. On the other hand, if it is properly performed the test is extremely delicate, and will give comparative results upon the same document of considerable value. A portion of the suspected ink is removed and a portion of that known to form a genuine part of the document. The two chloride tests should be run side by side. If any marked difference is noted in the diffusion of the chloride stain, the writing is of different periods. The migration of the chloride is, in our view, of no value except as a comparative test between portions of writing upon the same document.

Diffusion of Sulphates.—This is also true of the test for sulphates (*p.* 94). The test is less delicate than that for chlorides and its manipulation more complicated. But in inks which contain appreciable quantities of sulphates results of some precision can be obtained. In this case, as in the case of chlorides, comparative results are the only ones upon which reliance can be placed. The rate of diffusion is profoundly affected by the moisture of the paper, the temperature and probably by other factors which have not been determined, but where the tests are made upon the same document, and where other factors are constant, comparative results can safely be interpreted.

Colorimetric Method.—Mitchell has shown (*Analyst*, 1908, *xxxiii*, 80 ; *ibid. xlv*, 247) that thin washes of iron gall ink with provisional colouring matter attain their maximum intensity of colour in about a week. Thicker layers corresponding to those made with a pen require much longer periods and if light is excluded may require eight to ten months to attain maximum coloration.

The colour of suspected ink should thus be determined with a comparison microscope against Lovibond's standard colour scale. If it is found that the coloration increases rapidly the ink is comparatively fresh, and if it increases in colour at all within a fortnight the conclusion would be that it was less than eighteen months old. If on the same document certain portions of the ink darken whilst others do not, the ink is not contemporaneous. In cases where the date of the document is in question a colorimetric determination should never be omitted since it in no way alters the document and it may supply evidence of great value.

(h) Sympathetic Inks

There are different ways in which sympathetic inks can be classified, but the following scheme is generally representative.

(1) Substances which absorb or mechanically attract reagents so that the writing becomes visible by means of a mechanical effect.

(2) Substances which interact with the paper and alter its colour so that the writing becomes visible.

(3) Substances which react with chemical developers to produce coloured compounds.

(4) Substances which react with developers producing compounds which are developed visibly with another developer.

(5) Miscellaneous.

(1) **Mechanical Effect.**—All writing made with secret ink mechanically disturbs the paper, and/or leaves some deposit upon it. Theoretically, therefore, all writing in sympathetic ink should be made visible by absorptive agents or those which react mechanically. In practice the traces may be too slight for development to be effected mechanically.

(2) **Colour Change of Paper.**—Inks which change the colour of the paper are various types of acid urine, milk and a number of inorganic salts.

(3) **Simple Development.**—Substances which react with developers to produce coloured compounds include two general types, oxidizing or reducing agents.

(4) **Double Development.**—Reaction with the first reagent produces a water insoluble compound. This is made visible with the developer proper.

General Principles of Development.—Primary methods of development are those which rely upon mechanical effects. The effect may be induced either by wet or dry methods. Wet methods rely upon differential absorption of the reagent. Dry methods depend upon the actual adhesion of the developing material to the writing.

Wet Methods.—Iodine solution, alizarin and methylene blue solutions are examples of wet method reagents. A simple solution of iodine in potassium iodide is not, however, sufficiently sensitive as a developer. A preparation recommended by Locard greatly increases the differentially absorbent effect of the iodine:

Potassium iodide	4 gm.
Iodine	0·1 gm.
Sodium chloride	5 gm.
Aluminium chloride	2 gm.
Glycerine	3·5 gm.
Water	30 cc.

In making up the reagent the aluminium chloride must be added cautiously or the reaction may be very violent. This developer is a sensitive indicator of disturbance of the paper produced by secret writing. It is, of course, equally sensitive to accidental abrasions and local damage.

The mechanical action of alcoholic solutions of dyes such as alizarin and methylene blue is somewhat different. In general these reagents are absorbed by the material composing the ink itself. They may, therefore, be more satisfactory for the development of inks which produce very little mechanical damage to the paper. Conversely, certain inks repel the reagent so that the paper is stained and the writing remains colourless.

Iodine can also be used as an aqueous vapour. There are circumstances in which this form of development is very sensitive. The reagent consists of a concentrated solution of iodine in potassium iodide. The solution is boiled gently and the paper exposed to the vapour.

Dry Methods.—Iodine can also be used as a sublimate. The most satisfactory method of application is by means of an iodine " blower." This consists of a tube drawn out at one end to form a nozzle. The wide end is fitted with a cork carrying a piece of glass tubing to which a rubber bulb is attached. A glass wool plug is introduced into the tube at the nozzle end, about 2 gms. of iodine and a second plug of glass wool. The cork is then replaced. The heat of the hand round the tube while the air is blown through is sufficient to sublime the iodine.

This method of applying iodine is in many cases very satisfactory since it does not stain the paper severely and the stain produced disappears spontaneously.

Other methods of dry development depend upon the application of finely divided coloured powders. These mechanically adhere to the writing and thus make it visible. An essential property of these powders is that they should be of very small and of uniform particle size. Their chemical composition is of no importance. They may be either organic or inorganic, but in general oxides of the heavy metals are the most satisfactory.

Development by Heat.—Substances which dehydrate cellulose can be developed simply by heating the paper. The paper is thus slightly charred or discoloured and the writing consequently made visible.

Chemical Development.—Chemical methods are secondary forms of testing because they involve greater alteration of the document. They rely upon treatment of the ink with a reagent which produces a coloured compound as a result of the reaction.

Oxidizing and reducing agents are two types of substances which can be discussed in general in terms of development. If the ink is an oxidizing agent treatment with potassium iodide-iodate mixed with starch will produce a blue coloration with it because of the liberation of iodine from the iodide-iodate by the oxidizing effect.

There are also certain oxidizing catalysts which are utilized as secret inks. Benzidine acetate becomes blue when oxidized, but unless its oxidation is accelerated by the presence of certain agents this change does not occur. But ammonium molybdate, blood, serum and some other organic materials act as catalysts even in great dilution so that the reaction is brought about.

If reducing agents are treated with a mixture of ferric chloride and potassium ferricyanide which is colourless, a blue colour is produced because of the formation of prussian blue. The reaction is very sensitive so that organic compounds which are reducing agents even in great dilution bring this reaction about.

Double Development.—There is no general method which can be applied to sympathetic inks requiring this method of treatment. The object of using inks of this type is, of course, to make development impossible except by a specific method which cannot be applied unless the composition of the ink is known. This is the main problem which arises in connection with the development of all sympathetic inks. In the very nature of the circumstances it is generally impossible to apply tests which will identify the inks. Various methods of procedure have been suggested which rely upon the application of primary tests and examination with ultra-violet rays. These are designed to indicate the nature of the compound which has been used. They are, however, obviously unreliable, and in the majority of cases can give no specific information at all. It is obvious that in general, resort can only be had to primary testing and perhaps to those chemical tests which depend upon oxidation and reduction reactions.

Many sympathetic inks, however, intended to respond negatively to primary testing are, in fact, revealed by these methods if the sensitivity of the primary reagents is sufficiently high. Sublimed iodine, moist iodine vapour or the iodine reagent described are the most suitable for general use.

(i) The Examination of Burnt Documents

There are circumstances in which it may be necessary to determine what has been written upon documents which have been burnt. The motive of the burning may be precisely to conceal what has been written, or may have been accidental so far as the document itself is concerned. In either case, however, the ability to discover what, in fact, has been written may advance the enquiry.

The examination of such documents calls for manipulative skill of the character possessed by the chemist although the treatment is not chemical in the narrow sense.

Effect of Ignition upon Ink.—Different types of ink are affected in different ways by ignition. Aniline inks are entirely decomposed and do not usually leave traces upon the paper which retain their identity as writing. Carbonaceous inks and iron gall inks, however, leave sufficient residue to make the writing legible if the charred paper is suitably treated.

The traces left by iron gall ink are the most marked. Ink of this kind on ignition leaves a residue of iron oxide which stands out in contrast to the ash of the paper.

When the document is merely charred, however, the writing is not clearly visible. The paper itself is carbonized and therefore remains black in colour. The ink being incompletely ignited is not completely oxidized and does not develop a colour in definite contrast to the paper.

Mitchell (*Science and the Criminal*) was the first to suggest the method of incineration. If the document is charred and black the incineration is continued until the paper is reduced to a white ash. The inorganic constituents of the ink are then completely oxidized and contrast clearly with the white ash of the paper.

The method requires careful manipulation and failure is not uncommon. It is desirable to carry out the ignition in a large flat-bottomed vessel of pyrex glass which should be covered except for a small opening. This is essential to prevent the destruction of the ash by air currents. The incineration should be gentle and should be continued until the ash is completely white.

Photo-chemical Methods.—It should be noted that the incineration method should not be used until every other has failed. Here, as elsewhere, the principle applies that a document, whatever its condition, should be damaged as little as possible.

Davis (Police Department, Washington) has devised a method which seems to involve photo-chemical principles. He has reported that charred paper when placed in contact with a rapid photographic plate in darkness reproduces an image of any writing upon it if the exposure is continued for a fortnight. It appears that the reaction upon the emulsion is produced by the paper and not by the ink. It would appear, however, that if a film is used in place of a plate the effect is reversed, the reaction taking place as between the emulsion and the ink.

These incompatible results cannot readily be explained. The present author has not attempted them experimentally, or in actual practice. In general, however, photographic methods, if applicable, are more satisfactory in practice since they involve no change of state in the document. This is particularly desirable when dealing with so fragile a material as charred paper. The method of incineration described is theoretically sound but there are grave manipulative difficulties which are inseparable from it. For this reason every possible precaution should be taken, and recourse should not be had to the method if less drastic treatment is likely to prove successful.

More Recent Methods.—As a result of experience gained in the examination of burnt and charred documents recovered from business houses destroyed by incendiaries during the war, considerable progress has been made in the deciphering of burnt documents.

Taylor and Walls (*Nature*, No. 3727, April 5th, 1941) describe an interesting method for the deciphering of writing upon charred paper. They first treat the paper with a 25% solution of chloral hydrate in alcohol. The process is repeated several times, and the paper is dried at 60°C. between each application of the chloral hydrate. The result of this treatment is that a mass of crystals is deposited upon the charred surface. The paper is then treated with a similar solution to which 10% of glycerin has been added.

As a result of this treatment the charred surface is " clarified " and the writing becomes visible. It would appear that the most satisfactory results are obtained with typewriting and printing, but that ink writing can also be restored in this way.

The present author has found this method very satisfactory.

It is an interesting fact which has not been sufficiently recognized that at least in many cases the writing upon a document is not obliterated by charring. The reason it is undecipherable is the shrinkage and crinkling produced by burning has so distorted the characters that they cannot be read or even seen. If the charred surface can be flattened, the writing frequently becomes legible without treatment of any kind.

The present author has used the following method on a large number of documents with considerable success. A piece of thin cardboard is treated with an even layer of good dextrinous paste of the same area as the charred paper to be mounted. The charred paper is then laid gently on the pasted area, and a piece of heavy plate glass is then held about a quarter of an inch above the charred surface. It is then dropped on to the paper. The plate glass is left in contact with cardboard and paper until the adhesive is dry.

The result of this process is completely to flatten the charred paper, and whilst it is fractured often over the entire surface, the fragments fit together intimately if the plate has been lowered without any sliding motion.

In our experience typewritten documents invariably become readable if treated in this way. The method is less satisfactory in the case of ink writing.

If there is writing on both sides of the document, it can be mounted on fairly stout cellophane in place of cardboard, but this is less satisfactory. When dealing with documents written on both sides, Taylor and Wall's method is more suitable. Both sides of the document are " clarified " by treatment with chloral hydrate.

(j) The Examination of Subsidiary Materials

Besides ink or pencil and paper, documents are sometimes associated with subsidiary material such as wax or gum. In the case of anonymous letters and fraudulently manipulated envelopes an examination of these subsidiary materials may become important.

Sealing Wax.—Sealing wax consists essentially of a mixture of resins and mineral colouring matter. Since it is used in fairly large quantities for sealing letters or parcels it is generally possible to secure sufficient to make an analysis. The melting point should be taken, the ash determined, the resins and the colouring matter noted.

Melting Point.—Lucas recommends floating a small portion of the wax upon a little mercury in which a thermometer is immersed. The mercury is heated by means of an oil bath, the temperature of which must be raised slowly with a small flame.

Resins.—The wax must be reduced to a fine powder in a mortar with a pestle. It is then extracted with hot alcohol. It is usual to estimate the resins by difference by weighing the exhausted residue.

The resins can further be identified by their behaviour to different solvents thus :

Shellac.—Soluble in alcohol. Almost insoluble in benzene and ether.

Turpentine.—Soluble in alcohol, carbon bisulphides, and benzene.

Sandarac.—Soluble in alcohol and ether. Almost insoluble in benzene.

Rosin.—Soluble in alcohol, ether, and carbon bisulphide.

Dammar.—Partially soluble in alcohol, methyl, alcohol and ether. Soluble in benzene.

Copal.—Partially soluble in benzene.

Shellac and sandarac being insoluble in benzene are thus separable from the benzene soluble dammar and copal. The insolubility of shellac in ether also serves to distinguish it from the other resins.

Resins can be identified by adding a small quantity of acetic anhydride to a little of the wax in a test tube. The mixture is boiled, cooled, and a few cc. are transferred to a small porcelain dish. If a drop of sulphuric acid is added a red-violet colour develops if resin is present.

Examination of the Pigment.—The red pigment of sealing wax generally consists of vermilion (mercuric sulphide). There is a so-called vermilion substitute which consists of red lead (Pb_3O_4) coloured with tetrabromo-fluorescein (eosin). Red sealing wax may thus contain either mercury or lead.

Estimation of Mercury.—The sealing wax is treated with *aqua regia* which destroys the organic matter and dissolves the mercuric sulphide. The method of electrolysis is the most satisfactory for the estimation of mercury. The cathode, however, must be of gold or of platinum, heavily gilded. The solution must be slightly acid.

Bamberger, Feigl, Stock and others have utilized the reaction of diphenyl carbazone with mercuric salts. The coloration produced is blue-violet and the reaction is said to be quantitative. The present author has found the estimation very difficult in practice. A careful pH control is necessary, and it should be between 6·5 and 8. The results, however, are not, in our experience, consistent. If, however, only small quantities of the wax are available, no other method of estimation will give more satisfactory results.

Estimation of Lead.—The wax is treated with strong nitric acid to oxidize the organic matter. The solution is evaporated to dryness and the lead estimated as sulphate after precipitation with sulphuric acid in the usual way.

Comparative Analysis.—For the purposes of comparison, Mitchell (*Documents and their Scientific Examination*, *p.* 187) estimates total ash, ash insoluble in hydrochloric acid, the sulphates, the resins, and the pigment. This scheme of analysis is sufficient to identify a given sample.

In the case of Rex *v.* Fink (*Mitchell*, loc, cit.), this scheme of analysis was used to distinguish various samples of sealing wax and to show the correspondence between sealing wax found in the possession of the defendant and that of certain seals found upon documents in question.

It was clearly established that the defendant's wax was identical with that found upon these documents.

THE EXAMINATION OF GUM

The adhesive materials used upon envelopes are of a very varied character both in regard to their basic constitution and in the nature of the subsidiary material composing them. The adhesive material itself is of two general types, animal and vegetable. The animal adhesives, so-called glues, are hydrolytic derivatives of nitrogenous tissue. These adhesives normally harden on cooling but they can be retained in a liquid state by the addition of acids, calcium chloride, and zinc salts. Some vegetable adhesives are produced from proteins or alkali-proteins associated with the oils from certain seeds. These are treated with the hydroxides of the alkaline earths or magnesia and with such salts as sodium fluoride or arsenate which, by hydrolysis and interaction with the bases liberate sodium hydroxide. Proteins of the casein type are also used mainly for the preparation of " cements " but also in certain viscous types of adhesive. The third type of vegetable adhesive is that which is prepared from starch or dextrin. These are often in the form of pastes. For the most part, however, vegetable adhesives consist of dextrin, gum arabic, and starch pastes of various types.

Reaction of Gum.—It is an important fact that with the exception of some adhesives made from starch, gums are never neutral. The animal adhesives are generally acid ; those with a casein base are alkaline. The vegetable bases commonly used in adhesives for correspondence are also acid. A determination of the pH value with suitable indicators should thus always be made. Even a small difference in the pH value of the adhesive on a questioned envelope from that upon a control of the same type may in itself be conclusive evidence that the envelope has been regummed. If there are gross differences in the reaction, it may be positively assumed, in the absence of special conditions which might influence the result, that there has been manipulation.

Sodermann applies the following tests to identify various adhesives :

ANIMAL ADHESIVES

Common Glue.—Has an acid reaction. If heated on platinum foil it burns with a characteristic and unmistakable smell.

Albumin.—Also produces an acid reaction. If a small quantity is dissolved in acetic acid and potassium ferrocyanide is added, a heavy precipitate is formed.

Liquid Animal Adhesives.—These are also generally acid in reaction since they are prepared with acids or with calcium and zinc salts. The appropriate acid radicles are sought.

Nitric Acid.—The test recommended is that with diphenylamine which produces a blue colour in the presence of nitric acid or nitrates.

Acetic Acid.—Ferric chloride produces a maroon precipitate of ferric acetate which is insoluble in the viscous medium.

Oxalic Acid.—With calcium chloride a white precipitate of calcium oxalate is produced.

Boric Acid.—The presence of this acid can be detected by its reaction with turmeric paper.

Zinc Salts.—The presence of zinc is shown by its reaction with potassium ferrocyanide with which it produces a voluminous white precipitate.

Casein Adhesives.—Casein adhesives are alkaline in reaction and usually strongly so. Casein gives a pink coloration with Millon's reagent.

VEGETABLE ADHESIVES

Gum Arabic.—The reaction of this adhesive is usually acid by reason of the presence of formic acid present in it as a preservative. In spite of this yeasts and moulds are generally found in it and can be identified microscopically. The ash of gum arabic is alkaline. The alkalinity is due to carbonates which can be identified by the usual test.

Starch Pastes.—These commonly consist of wheat, rice, or maize starch. The type of starch is identified microscopically. The classical test with iodine should be applied in the first place.

Starch adhesives are of two types. The pastes are neutral, but liquid starch paste is acid in reaction. If the adhesive is found to be acid, the acid radicle should be sought by the usual tests.

Dextrinous Adhesives.—Those of good quality are white and acid in reaction. Most dextrinous adhesives give the starch reaction with iodine. They reduce Fehlings Solution. Dextrinous adhesives of poorer quality are brown. They are acid in reaction and reduce Fehlings Solution.

Interpretation of Results.—If sufficient of the material is available, it is generally possible to identify the adhesive by means of these tests if they are systematically applied. The object of the analysis is usually to compare the gum upon a suspected envelope or stamp with that of a standard known to be genuine. The results can readily be interpreted since marked differences in the result always point to falsification. It is not uncommon to find, for example, a starch reaction in an adhesive whilst the genuine standard shows no such reaction. This indicates that the envelope or stamp has been regummed with a starch or dextrinous paste.

(k) The Development of Skin Prints on Documents.

First, the development of skin prints on documents must be attempted only in certain circumstances. A good deal of damage can be done to a document in an attempt to develop prints. If it is to be examined for forgery the establishing of the fact of falsification or the reverse is the first consideration. Nothing must be done which is likely to interfere with this process. Since the development of skin prints usually involves an extensive area of attack, it is obvious that the treatment may interfere with the more important examination. Inexperienced examiners can also reduce the document to such a condition that its production in court will result in disputes prejudicial to the enquiry.

Secondly, the results even if technically successful may be impossible to interpret because the document in question has been extensively handled and in consequence carries a number of skin impressions which have no bearing upon the enquiry and may actually conceal the evidence sought.

Thirdly, on the other hand, documents such as some anonymous letters which have not been forged can often be usefully dealt with in this way provided that proper precautions are taken with the examination.

Types of Impression.—Finger-prints, palm-prints, and exceptionally impressions of the lips and other parts of the body may be found upon documents. Lerich, *juge d'instruction* of Lattaquié, has reported the case of the correspondence of a Syrian prostitute who was accustomed to impress her letters with the lips, leaving a visible pattern due to the lip salve. Claps (*Rev. Inter. de Crim.*, 1931, 9, 704), after a detailed and elaborate study of lip prints concluded that:

> L'empreinte labiale ne pourrait guère être utilisée, en criminalistique, que pour la reconnaissance des individus, dans le cas ou l'on n'aurait à sa disposition ni des empreintes digitales, ui des marques particulières permettant une identification.

In regard to other impressions in a case where it was known that a French prostitute was in the habit of applying certain of her correspondence to the vulva, attempts were made in our laboratory to develop the impressions without much success. In regard to the identification of such impressions, see also Locard (*Traité de Criminalistique*, *I*, 445). Whilst these questions are of considerable theoretical interest, in practice the development of finger and palm impressions and occasionally those of the feet are the only ones of importance.

Development of Skin Prints.—Lerich (*Rev. Inter. de Crim.*, *April*, 1932) has successfully developed both finger- and palm-prints upon Syrian documents. In the same paper he also reports an interesting example of the development of the prints of a fingernail upon a document which was identified as that of the auricular finger. In any case the author has conclusively shown that both finger- and palm-prints can be developed upon documents and identified with sufficient frequency to make the method of value in criminalistic practice.

Method of Development.—Methods of development of finger-prints on paper have already been described (*p.* 4 *et seq.*). The reagents commonly used in practice are iodine, iodine and aqueous vapour, osmium tetroxide (Mitchell), and ruthenium tetroxide.

Locard (*Traité de Criminalistique, VI,* 773) has recommended a special preparation of iodine which he describes as nascent iodine. Iodine is liberated from potassium iodide by mixing the iodide with manganese dioxide in hydrochloric acid. Liberated iodine in this form is a very sensitive developer. It has the further advantage of disappearing rapidly, leaving the document essentially unchanged.

Photo-chemical Development.—Development with silver nitrate is the most sensitive method, but it has certain features which make it unsuitable for use on documents. The prints are permanent and if many exist on the surface the paper may be severely stained in a number of places. Further, it must be noted that a silver developer may fail where others would succeed. The reason is that this developer utilizes the chloride only: Owing to the migration of the chloride the print when developed may be too faint for identification. Fresh prints are thus the only ones which can be developed by this method. Once recourse has been had to this method it is not possible to redevelop by other means.

In our experience, development with iodine freshly liberated from potassium iodide is the best method of development in all but exceptional cases. The use of iodine in aqueous solution of potassium iodide from which the iodine is liberated by heating gives satisfactory results, but it has the disadvantage of acting upon the ink of the written document.

CHAPTER VI

THE CHEMICAL EXAMINATION OF COUNTERFEIT MONEY

(a) Counterfeit Banknotes

THE forging of banknotes has become of recent years an occupation which requires considerable skill and knowledge of printing and engraving. Chemical examination is generally of little use in examining documents of this kind except so far as a chemical examination of the paper may be necessary.

There is, however, another type of counterfeiting which is still very popular, namely, forgery of notes by free hand drawing or tracing. When the work is undertaken by skilled draughtsmen, as it frequently is, the results are often the production of a counterfeit note which is superficially indistinguishable from the genuine note. In England and in most civilized countries, vigilance in connection with forgery is so great that clumsy counterfeiting would be immediately detected. The result is that inefficient work is rare, and a high percentage of forged notes shows a great degree of technical skill.

Whilst the examination of printed or even drawn banknotes ought in general to be undertaken by an expert with an intimate knowledge of the manufacture of genuine notes, chemical examination may in certain circumstances be of assistance. The chemist should in any case acquaint himself with the methods used in printing banknotes for the same reason that he should acquaint himself with the composition of writing materials and paper. He should do this if only to avoid the undertaking of an examination he is not qualified to perform. In the Portuguese Banknote Case, for example (*Rhodes*, *The Craft of Forgery*, 1934, *p.* 182), the examination of the disputed notes was entrusted to experts in engraving, employed in England and Portugal. The experts employed were alone qualified to make an authoritative judgment.

Colorimetric Examination.—The colorimetric examination with a comparison microscope may in some circumstances give information of value. Differences in colour must not, however, be interpreted rashly. Genuine notes may and sometimes do vary in colour from printing to printing. This was shown to be the case in the Portuguese Banknote Case (*Rhodes*, loc. cit.). On the other hand, differences in colour should be carefully recorded since if they are marked, the circumstance is always suspicious.

Hand-drawn Forgeries.—A micro-chemical examination of the ink may provide valuable evidence in the case of hand-drawn forgeries. Five and ten pound notes which are extremely accurate copies of the originals can be produced with a mapping pen and chinese ink. If carbonaceous ink of this type is identified by micro-chemical tests, the forgery is established.

In the case of hand-drawn forgeries generally, the same technique of micro-chemical examination should be applied as in the examination of written documents. The coloured inks used are usually of the ordinary aniline type and present no special difficulties of identification not associated with ordinary ink-written documents. Chemical tests with dilute acids and bleaching agents distinguish sharply between printing inks used on genuine notes and the writing inks used by the free-hand forger, so that positive conclusions can nearly always be drawn.

Forged Watermarks.—Forged watermarks are produced by the preparation of a rubber stamp of the design of the mark it is desired to imitate. The stamp is then moistened with a wax or a drying oil, and it is pressed upon the paper using a firm and even pressure. The imitation if examined in detail is generally found to be defective.

A conclusive test is treatment of the suspected watermark with a solvent such as ether. Since ether-soluble substances are invariably used for this type of counterfeiting the material forming the watermark will dissolve. If this occurs, the watermark is not genuine.

Examination of the Paper.—The paper of genuine bank-notes is always of high quality. In no case in our experience has a counterfeit note matched even approximately the paper of the genuine note. The chemical tests already described (*p.* 102) can be applied. Lucas (*Forensic Chemistry*, *p.* 83) employs, besides iodine and zinc-chlor-iodine, phloroglucine and aniline sulphate. These reagents give red and yellow colorations respectively with mechanical wood paper. The reactions are negative with linen, straw, cotton, esparto, and chemical wood.

Tests of this kind may not be conclusive since the paper of the forged and genuine notes may be of the same cellulose type, and yet of different quality. At the same time, the chemical tests should not be neglected since they may prove important evidence of identification if the paper of the forged note is found to be of the same composition as that of paper found in the possession of a suspected person.

Seizure of Suspected Materials.—In cases of note forgery it is of vital importance, first, to get the counterfeit notes out of circulation as soon as possible, and, secondly, to trace without delay the origin of the forgeries themselves. Where hand-drawn forgeries are concerned in particular a chemist should co-operate with the police in the conduct of the search of suspected persons and premises. Bottles of ink, draughtmen's materials and paper should all be carefully scrutinized, packed, and taken to the laboratory for examination. The source of the forgeries may be conclusively established in this way.

Forgery by Tracing.—As with other forged documents the bank-note design may be reproduced by tracing and the inking over of the traced model. The tracing may be effected by the use of carbon paper, or as is more common, by a direct pencil tracing carried out on a " forgery table " (a glass-topped desk with a strong light beneath).

The chemical examination in this case aims at exposing the underlying pigment with which the tracing was effected. For this test the ink is treated with acid, 10 to 20% in strength, which removes the ink but leaves the pencil pigment unaffected. The demonstration that the design was traced in pencil is, of course, conclusive evidence of forgery.

(b) The Examination of Counterfeit Coin

General.—The chemical examination of counterfeit coin forms a very important part of any enquiry into coining. Unlike an enquiry into many other crimes, the object of the investigation is not only the detection of the criminal but the discovery of the real nature and extent of his work. Forgery and counterfeiting are peculiar in this—that a considerable period of time may elapse before it becomes evident that a crime is being committed at all. Even when this is known, the extent of it may be largely a matter of surmise. Primarily, at any rate, these considerations are more urgent even than the detection of the coiners. It is necessary to discover first if the counterfeiting is being carried out on a large or small scale ; secondly, in what areas the money is circulating ; and thirdly, if all the counterfeit money is emanating from one source.

Chemical analysis of the coins themselves is usually the most convenient method of deciding the third point, although there are various methods of physical examination by which counterfeit coins may be identified. The same group of coiners may, however, produce coins which show physical variations. A change in chemical composition generally indicates conclusively that different groups are at work.

Conclusive proof of the discovery of the source of the coins may depend upon chemical examination. If the material found at the suspected source proves to be of the same chemical composition as the coins it is obvious that the source has been located.

Occupational Dust.—The question of occupational dust is also of importance. It is not uncommon to find metallic fragments associated with the clothing of coiners, which may even agree substantially with the composition of the coins themselves. The establishing of a fact of this kind may be vital in certain circumstances. It is a common defence of the coiner that he had unintentionally passed counterfeit coin but had not manufactured it. If it can be shown that the clothing carries even traces of the raw material from which the coins are made, this is conclusive evidence that the suspect has been associated with the manufacture.

Plaster of paris (*infra*) may also be associated with the clothing of coiners. The source of this is the moulds from which certain types of counterfeit coins are made.

Methods of Manufacture.—There are essentially two methods of manufacture of counterfeit coins, namely, production by moulding and striking from dies. It is, of course, possible to produce coins by the electrotype process, but this method is seldom if ever used. In practice the coins are moulded or struck, moulded coins being by far the most common in England and Europe generally.

Dies require considerable skill for their manufacture and have to be prepared by an engraver. They may be cast and then finished by engraving or engraved direct. Coiners who produce stamped money are well organized and even command the services of skilled engravers and mechanics. Cases are on record where dies and stamping machinery were almost equal to that employed by legal mints. An example is the plant produced by Bonnot (*Locard*, *Traité de Crim.*), whose dies and stamping machines were of the best quality. Where the work is of a high standard the coiner works not on the original die but upon secondary dies prepared from the master engraving. Owing to the high standard of workmanship and the consistent result produced, the difficulty of detection is increased. On the other hand, the plant is cumbersome and cannot readily be disposed of. It is, in this way, a considerable danger to its possessor.

For this reason moulded coins are much more common. The process of manufacture is simple. The mould is small and it can be destroyed at a moment's notice. It consists of a superior and inferior part made of plaster of paris which is moulded, using a genuine coin to produce the impression in reverse and obverse of the coin. The two parts of the mould fit closely but a groove is made in one section to allow the expulsion of the excess of metal. The coin is made from an easily fusible alloy which is melted and poured into the mould. The second section is placed in position and pressed down, the excess of metal escaping through the vent made by the groove. The milling is, of course, reproduced in the mould, but it has to be finished with a file. With skilful manipulation, very good reproductions can be produced by this method. All such coins, however, show minute faults by which they can often be identified as coming from the same mould.

THE COMPOSITION OF COUNTERFEIT COINS

Counterfeit coins vary greatly in composition. In the first place the stamped coin is naturally of greater hardness and tensile strength than the moulded coin. It is, in fact, by no means unknown for counterfeit coins to be of the same composition as genuine currency since it is sometimes possible for counterfeiters to take advantage of favourable movements in the price of metal and so manufacture coin more cheaply than the official mint. This is exceptional, but in the case of Bonnot (*Locard*, loc. cit.), the technical police seized a large number of unstruck discs which upon analysis proved to be of the same composition as the contemporary French coin.

The quantity of silver in English coin is now the same as it was in the fifteenth century. It contains 7·5 % of copper (fineness of 925). French silver coinage used to contain 10 % of copper (fineness 900). The German coinage also contained the same quantity of silver as the French.

In countries which still employ silver coinage these facts are of some importance. The highest quality of counterfeit coin contains a reduced quantity of silver with copper and the addition of nickel and tin to replace the loss of the silver. Suitable alloys of this type if well struck are very difficult to detect by inspection.

Moulded coins always contain a high percentage of lead since they must be made readily fusible. The usual constituents of moulded coins are antimony, tin, and lead. In those of better quality the percentage of lead is reduced as much as possible since the coin rich in lead rapidly becomes discoloured and takes on a greyish tint which cannot be easily mistaken once it has been observed.

Coins of this type have silver deposited upon them electrolytically. For the time being this gives them a superficially genuine appearance. By reason, however, of galvanic action, the silver coating quickly wears off, exposing the greyish surface underneath.

Indirect Evidence supplied by Analysis.—In no kind of forensic enquiry is the co-operation of the investigating officers and the laboratory more important than in the case of counterfeit money. The chemist should request that every sample submitted to him for analysis should include particulars of the area in which the counterfeit coin was found. If this information is available, it may be possible to map the areas where different types of coin are being made or trace the movements of the distributors or of the coiners themselves. Without data concerning the composition of the coins, it is much more difficult for the investigating officers to trace their movements. If this cannot be done, it is not possible to trace the movements of the coiners themselves. The significance of this must be emphasized. Forgers of notes and coiners often continue their work for two or three years before they are detected ; a few have enjoyed immunity from arrest for as long as ten years. A systematic correlation of the identity of the counterfeit material (supplied by analysis) and the area in which it is found may shorten the enquiry considerably.

ANALYSIS OF COUNTERFEIT COIN

Colour.—The colour of the surface should always be carefully noted since this in itself may be a means of identifying similar coins. Counterfeit coin is often yellow or grey. A yellow tinge may be due to an excess of copper or to the sulphiding of the alloy. On the other hand, coins with an excess of lead have a leaden appearance which reflects very little light. Abnormal coloration does not always indicate a lack of genuineness. Silver which has been mixed with copper coins may develop an abnormal coloration which appears suspicious at first sight.

Weight and Specific Gravity.—These physical characteristics must always be recorded. If the coin is found to be heavier than the legal mint of the genuine coin, it is certainly counterfeit. The weight of genuine coins is so carefully controlled that they never exceed a certain limit. On the other hand, a defect in weight is much less conclusive since it may be due to wear. If, however, the coin shows little sign of wear and is defective in weight, it is a very suspicious circumstance.

The figures of density of the coin must be interpreted with caution. Differences in density between two coins do not necessarily indicate that they are composed of different alloys. Coins of the same size should be of the same density, but the density is inversely as the size of the coin. The reason for this is that a constant crushing strength has a greater effect upon a more limited area.

The density of counterfeit coins may bear an even less definite relation to their composition. The stamps may vary greatly in efficiency so that alloys of the same composition show wide variations in density. The density of the moulded coin is more consistent since the treatment does not bring about a variable change of state.

DETECTION OF METALS

The metals which may be found in counterfeit coins are the following in order of their frequency. Lead, tin, antimony, zinc, nickel, copper, aluminium, iron, silver, gold, chromium, tungsten, and bismuth. Iron, gold, tungsten, and bismuth are rarely present except as impurities, but their presence even in minute amounts may be important for the purposes of identification.

It is advisable to make a qualitative analysis before proceeding to the estimation of the metals. Only in exceptional cases are more than three metals present in any quantity. In the case of moulded coins the alloy will almost certainly consist of antimony, lead, and tin. Traces, at least, of silver will also be found due to silver plating. Copper and tin will probably be present in struck coins with or without silver. Nickel may also be present.

It is advisable, however, to proceed systematically with the classical group separation since this is generally the most certain and rapid method of ascertaining the nature of the alloy.

Detection of Impurities.—Where traces of impurities are sought, however, the spot reactions may be applied.

Where traces of bismuth, silver, or gold are suspected, for example, the hexamethylene tetramine micro-chemical test may be applied.

Antimony, if present in large quantities, should be removed. The solution to be tested should be only slightly acid. A fragment of the solid reagent should be added to a drop of the test solution on a microscopic slide, and the drop stirred with a fine-pointed glass rod.

Bismuth.—Forms colourless and highly refractive octahedra and dodecahedra of the isometric system. If potassium iodide is added yellow octahedra are formed.

Gold.—Forms pale yellow needles or plates showing strong polarization with parallel extinction.

Silver.—Produces colourless needles or plates of the monoclinic system.

Tungsten.—The reaction with benzidine may be used for the detection of this metal. The solution should be neutralized and then made acid with 0·1 N sulphuric acid. The reagent consists of a 2% solution of benzidine in 1% hydrochloric acid.

Slight excess of the reagent is added to the test solution. In the cold and on standing a precipitate of benzidine tungstate and benzidine sulphate is formed. The reaction is quantitative. It is essential that distinct excess of sulphuric acid is present since this facilitates the precipitation of benzidine sulphate. The object of the formation of the mixed precipitate is that the benzidine tungstate alone clogs the filter paper and may render the solution practically unfilterable.

QUANTITATIVE ANALYSIS

Iron, copper, lead, antimony tin, zinc, and silver are the metals which most commonly require to be estimated.

The samples for analysis should be taken by making drillings of the coins at various points and mixing the drillings made from which the sample to be analysed is taken. Fair sampling cannot be assured unless this is done. If more than one coin is available drillings should be taken from each coin and the drillings mixed. If sufficient material is available about five grams should be taken for analysis.

Iron.—The iron can be estimated in the usual way by precipitation as ferric hydroxide and incineration to ferric oxide. The precipitation should, however, be made with potassium hydroxide if traces of aluminium are suspected. The precipitate is redissolved in hydrochloric acid and precipitated with ammonia.

Copper.—The copper can be precipitated with hydrogen sulphide and weighed as cuprous sulphide. Alternatively it can be determined by iodometry which is in our experience the most satisfactory method for its determination in counterfeit coin.

Lead, Antimony and Tin.—These metals are usually found in conjunction in coins which have been made by moulding. Other metals are not usually present except in traces as impurities. They are estimated by the methods already described.

Zinc.—This metal is most conveniently estimated in counterfeit coin volumetrically with potassium ferrocyanide. Excess of potassium ferrocyanide is added to the dissolved metal in slightly acid solution. The excess of potassium ferrocyanide is then titrated back with a standard solution of zinc in hydrochloric acid using uranium acetate as indicator. Alternatively, the zinc may be titrated direct with potassium ferrocyanide. Back titration gives a sharper end point.

Silver.—This metal should be estimated by precipitation as chloride with hydrochloric acid, the usual precautions being taken to avoid excess of acid and reduction of the silver chloride by exposure to strong light.

It must be noted that these methods give a general indication only of the procedure to be followed. The composition of the alloy from which the coins are made may make the separation of interfering metals necessary. Bismuth, nickel, and copper, for example, interfere with the volumetric estimation of zinc. One of these metals may form part of a coin alloy containing zinc. It is for this reason always advisable first to make a complete qualitative analysis of the alloy so that the necessary separations can be effected before the quantitative analysis of a given metal is undertaken. It is rare, however, to find more than three metals as the main constituents of a coin alloy. Others may be present as impurities although often in such small quantities as not to interfere.

Dusts.—Since in cases of coining occupational dusts and those of location are very characteristic a careful examination should be made of the clothing of all suspected persons and of the dust and débris found at the suspected place of manufacture. The evidence is, of course, conclusive if specimens of the alloy itself are found, the analysis of which agrees with that of the coins. The presence of lead and tin alone is suspicious, but might be explicable on other grounds in the absence of confirmatory evidence. Metallic occupational dusts are associated with other workers such as mechanics and fitters. In one case within the author's experience, the coiner was a foreman mechanic who actually produced his counterfeit coin on the premises where he worked. On these premises metals were to be found which served both a legitimate and illegitmate purpose. The coiner in question was, in fact, arrested *in flagrante delicto.* In this case, the circumstantial evidence supplied by an examination of occupational dust would clearly have been inconclusive. This will serve as an indication of the caution which is necessary in the interpretation of this kind of evidence if all the surrounding circumstances are not known.

The presence of calcium sulphate may sometimes be detected in association with metals from which counterfeit coins might have been made. If this substance is found it is always highly suspicious.

If traces of potassium and silver cyanides are found either in clothing or elsewhere this will indicate that silver plating has been undertaken. If these substances are found associated with other materials belonging to the act of coining it is strong presumptive evidence that counterfeiting is being carried on.

CHAPTER VII

THE EXAMINATION OF TOXIC AGENTS

General.—The term toxicology includes more than the chemical examination of poisonous substances. Toxicology has been defined as including not only the chemical composition but the physiological action of poisons and their antidotes. Definition of the term is important because it is essential to recognize that there are many aspects of toxicology which do not fall within the scope of the chemist. There still exist a number of poisons which cannot be identified positively by chemical methods. The chemist is not concerned with the physiological action of poisons, nor with therapeutic properties possessed by many of them, nor with any clinical problem which their administration may present. This consideration is not merely academic. It is essential that the chemist should confine himself to the technique concerned with the chemical properties, the detection and determination of toxic substances.

Section II of the Offences Against the Person Act says that : Whosoever shall administer or cause to be administered to or taken by, any person, any poison or other destructive thing with intent to murder, shall be guilty of felony.

Section 23 says that : Whosoever shall unlawfully and maliciously administer to, or cause to be administered to, or taken by, any other person, any poison or other destructive or noxious thing, so as thereby to endanger the life of such person, or so as thereby to inflict upon such person any greivous bodily harm, shall be guilty of felony.

And Section 22 says that : Whosoever shall unlawfully apply or administer to, or cause to be taken by, or attempt to apply or administer to, or attempt to cause to be administered to or taken by any person, any chloroform, laudanum, or other stupefying or overpowering drug, matter, or thing . . . shall be guilty of felony.

The law makes a distinction between poison and a destructive or noxious thing. It has been held that a destructive thing means an agent which may cause death or injury by mechanical action. The term noxious has given rise to controversy. In the case of Rex *v.* Cramp (1880) the defence sought to show that an agent must be proved to be noxious in itself. Coleridge, L. C. J., ruled, however, that " if a person administers . . . something which, as administered, is ' noxious ' he administers ' a noxious thing.' "

These considerations have some importance from the chemical point of view. The chemist is not primarily concerned with the toxic properties of the substance but with its identification. The chemical aspect of toxicology is thus a problem of identification of material amenable to chemical analysis and not its effects upon the human organism.

The problem of identification is of two kinds. (1) The identification of the material sought independently and (2) its identification within the body. The first of these is of special interest in the forensic chemical laboratory. Toxic substances may be found on the scene of the crime either independently, on the person of the suspect, or associated with dusts or stains.

Classification of Poisons.—From the chemical point of view the classification of poisons is best considered in relation to their physical and chemical properties rather than on the basis of their physiological action. A poison may be either an inorganic or an organic compound, and it may be either solid, liquid, or gaseous. The ordinary physical condition of the substance may have a profound bearing upon the general technique to be applied for its identification. Solids, for example, may be found unchanged in the body and liquids may also occasionally so be found whilst gaseous poisons will require special technique for their identification. It is also true in general that inorganic substances are more readily identified than organic compounds which are more difficult to isolate, and are more readily confused with naturally occurring substances of metabolism or decomposition.

The chemist is entitled to acquire any information which is likely to assist him in his preliminary examination. He should ascertain, if possible, the symptoms from which the victim of the alleged poisoning suffered, and any other circumstances which may give him a clue to the nature of the toxic agent employed. As a matter of routine the chemist should be informed concerning:

(1) The time elapsing between the taking of the last meal and the appearance of the symptoms of poisoning or death.

(2) The nature of the symptoms.

(3) Whether there was (a) Vomiting and purging, (b) Deep sleep or coma, (c) Tingling of the skin, (d) Convulsions, (e) Delusions.

(4) The nature of other symptoms if any.

(5) Whether more than one person was affected and if so how many and to what extent.

(6) Any other information.

If information on these points can be supplied it will indicate what type of poison has been used and will facilitate the identification of the toxic agent.

Toxic Agents External to the Body.—When considering this question, it must be realized that the examination for *corpus delicti* of this kind includes much more than a search for bottles, packets or other normal containers of substances likely to be toxic. It may be necessary to investigate stains, dust, small traces of deposit found in utensils or in clothing. In special cases other types of investigation may be necessary. An example is the examination of a contaminated atmosphere which might have been the cause of poisoning. Normally an instance of this kind is outside the scope of criminal practice. But it may be associated with it. Thus, in the Lafarge case, it was held by the defence that the victim had died of arsenical poisoning, but that the source of the intoxication was accidental and due to the arsenically charged atmosphere in which the victim worked. Owing to the increase of chemico-industrial hazards it is obvious that circumstances may at any time arise making a special toxicological examination of this kind necessary.

The examination of dusts may also be of great evidential value. A classic instance of this is the famous Maybrick poisoning case. A detailed and systematic examination of the whole house was made for traces of arsenic. Whilst many of the deposits found were probably of accidental occurrence, traces of arsenic were found mixed with the dust in the dressing gown pockets of the accused.

In many cases the examination of stains may be of great significance. These are not necessarily connected directly with cases of poisoning. In vitrol throwing affairs a very minute examination of the clothing of the suspects may reveal stains which are identifiable as having been made by the acid used.

In cases of the procuration of abortion by means of drugs a meticulous search for traces and stains has to be made. The experienced abortionist is very careful not to leave obvious evidence of his or her activities, and the evidence may well turn upon the discovery and ability to identify small quantities of abortifacient material.

Toxic Agents within the Body.—Strictly speaking the examination of toxic agents within the body is a matter which cannot be dealt with without the co-operation of the pathologist. There are at the same time certain special preparations with which the chemist should deal.

It is very desirable that he should be responsible for the preparation of the receptacles in which material for toxicological examination is contained. The vessels should normally be wide-mouthed glass bottles with solid glass stoppers. They should be thoroughly cleaned with potassium dichromate and sulphuric acid and very carefully rinsed first with tap and finally with distilled water. They should not be dried with a cloth but allowed to drain. The chemist himself must supervise these operations, or better, do them himself.

If small samples of material have to be taken vessels of suitable size must be supplied to contain them. Samples contained in vessels of disproportionate size can give rise to great difficulties. Scrupulous cleanliness of the vessel is even more important where the sample is small.

(a) The Technique of Examination

The special technique of toxicological examination consists in the separation of the substance sought from the materials with which it is associated. When this has been accomplished the examination follows the ordinary course of examination appropriate to the compound to be identified. It is not appropriate to discuss here methods of toxicological examination discussed in other books. What is important is to consider the general principles of the analytical technique of toxicology and the manner whereby it is applied and adapted in the circumstances already described. Upon the adequacy of the preliminary steps taken the success of the examination may depend.

Two prerequisites are the use of chemically clean apparatus and absolutely pure reagents. Even with these precautions blank experiments should be run to check the purity of all reagents used. There is no kind of analytical technique in which the blank experiment is more necessary.

Preliminary Tests.—The extent to which preliminary tests can be applied depends upon the amount of material available. The first test is to note carefully the odour of the sample. A number of volatile poisons such as phenol, chloroform, and hydrocyanic acid can often be detected in this way. A practised nose is, however, an essential. The sample itself may have an odour which masks that of the poison, and alters its character. The experienced nose will, however, often detect the substance by its smell even when masked in this way.

The sample should then be tested with litmus paper and the reaction noted. A careful examination should then be made for the presence of particles of foreign material. Insoluble mineral substances, portions of leaves, seeds, or other vegetable débris may be detected. If foreign particles are detected they should be mechanically separated, washed, and more closely examined. Some of the material thus isolated may not be amenable to chemical examination. In this case it should be preserved for examination by the pharmacologist or botanist.

General Methods of Separation.—Lucas (*Forensic Chemistry, p.* 286) has classified toxic agents according to their behaviour when submitted to certain specific laboratory procedure. Thus, he divides poisons into four groups (1) Volatile substances which can be separated from the menstruum by distillation. (2) Non-volatile substances which can be extracted with solvents. (3) Substances which resist the action of oxidizing agents sufficiently to allow their use to destroy organic matter. (4) Special cases.

This classification is very valuable because it is founded upon the chemical behaviour of the substance in question ; and it is, in fact, true that the majority of toxic agents found in the body can be dealt with by one of these methods. Further, the methods in practice may actually reveal the identity of the substance or at least classify it and thus narrow the field of investigation. Lucas recommends the division of the sample into at least three parts. The first is used for distillation for the separation of the volatile substances, the second is used for extraction with solvents, and the third is retained as a control. When dealing with micro-quantities it is not always possible to divide the sample but where practicable it should be separated into at least two lots.

Separation by Extraction.- Certain special considerations apply to the application of the Stas-Otto principle of extraction upon a small scale.

As already indicated the first extraction with acidified alcohol can be carried out by simple digestion in a capillary of wide bore. It is often convenient, however, and may be necessary to reflux the alcoholic mixture. This can be done very simply by attaching to a bulbous capillary a second length of capillary tubing 12 to 15 cm. long inferior in diameter and of a size to fit snugly within the wider capillary. The mixture can then be heated in a water bath in the usual way.

It is neither advisable nor necessary to attempt filtration. The capillary is centrifuged and the extract removed by decantation.

It is not advisable to attempt near neutralization with sodium bicarbonate. With dusts or stains this procedure is not generally necessary. The first charge of acidified alcohol should be sufficient to ensure a faintly acid reaction.

Only one secondary extraction with alcohol should be made. This should be done in a capillary of wide diameter with a stirring rod so that the mixture can be stirred. With small quantities a complete extraction can generally be made with a single treatment with alcohol.

Evaporation or concentration of the alcoholic extracts is carried out with a current of warm air as in the other micro-operation. The dentist's blower can be used.

No special comment is called for in connection with the treatment with acidulated water.

If the presence of morphine and/or meconic acid is suspected and a separation is necessary, it is preferable to add a minute crystal of lead acetate rather than a solution of the reagent to the extract. If, however, it is practicable to divide the extract into three parts one of them may be tested for meconic acid with ferric chloride. The advantage of this is that if meconic acid is absent, the troublesome operations of the addition of lead acetate and the subsequent removal of the lead with hydrogen sulphide can be eliminated.

Where an ether or other fat-solvent extract of an aqueous solution has to be made, the problem of separation arises. This can be carried out in a sedimentation glass with a thimblelike depression in a glass tap at the bottom of the glass. A simpler and generally more effective method is to remove the ethereal extract with a capillary. This does not, of course, effect a complete separation, but this is not essential if a qualitative examination is being made. Care must be taken not to immerse the capillary too low in the ethereal layer. Also it is not easy to see the line of junction of the liquids in so thin a column. A watchmaker's lens which can be held in the eye is convenient for making the observation while leaving both hands free.

The ether and chloroform extracts which effect the separation of alkaloids and synthetic drugs can be separated in the same way.

It is thus practicable to apply the Stas-Otto or similar principle of separation on a micro-scale if qualitative tests of the material under examination are alone sufficient. The quantity of dusts, stains or residues which become available for investigation vary in quantity between wide limits. In favourable cases it may be possible to extract upwards of a gramme of dust from clothing and stains do not necessarily consist of micro-quantities. At the same time it is often necessary to be prepared to deal with quantities of the order of milligrammes. In such cases micro processes are not only convenient, but essential. When dealing with dust stains, and similar material micro- or semi-micro processes are still generally more convenient for qualitative tests even when macro-quantities of the sample are available. It is true of forensic chemical processes, as it is true of analytical technique in general, that the time is coming when micro-analysis will altogether replace the classical analytical operation.

THE MICRO-CHEMICAL IDENTIFICATION OF ALKALOIDS AND DRUGS

Alkaloids.—For the commoner alkaloids the classical colour reactions are still in use. The disadvantage of their application in microchemical practice is the variation in the sensitivity of the tests and the interference produced by impurities. This is a very serious factor on a micro-scale. As an example of sensitivity the test for brucine with nitric acid is of the order of 0·06 gamma, but few of the other colour reactions even approach this order of sensitivity and they are, in fact, unsuitable for use on a micro-scale.

More recently the chemico-microscopic reactions of alkaloids have been studied. It has long been known that alkaloids form insoluble crystalline addition products with a number of reagents. Gold chloride, mercuric chloride, and picric acid are typical examples. A classical crystallizing reagent is that of Marmé. Its composition is :

Cadmium iodide	3 gms.
Potassium iodide	6 gms.
Water	18 cc.

The reagent is mixed with an aqueous solution of the alkaloid. A crystalline precipitate is formed of a characteristic type which is recognizable microscopically. These compounds also have sharp melting points.

It is, however, most important to recognize that it is only under the most rigidly standardized conditions that this form of chemico-microscopical technique will give specific results. Conditions of concentration and temperature are much more influential in connection with the crystallization of organic compounds than in the case of inorganic compounds. On the other hand the crystalline forms are in general more readily recognized. This is because not only is the crystallographic modification characteristic, but in many cases the manner in which groups of crystals are clumped. Polarized or dark ground illumination may in some circumstances assist in identification.

Technique.—In the first place it is highly desirable that a chemico-microscopic control should be run alongside that of the test material. That is to say that if the presence of a particular alkaloid is suspected a micro-quantity of the pure substance should be tested under the same conditions as the test material. If the results of the two analyses agree, the inference is that the material has been positively identified. If the two analyses do not agree this does not necessarily show that the suspected substance is not present. This is because it may be associated with impurities which influence its crystalline form and the orientation of the crystal groupings themselves.

On a micro-scale, it is a matter of considerable difficulty to isolate a given alkaloid pure. For microscopical identification it is, however, necessary that the material sought should be as free from possibly interfering substances as possible For this reason a Stas-Otto type of extraction in the manner described is an essential preliminary to a chemico-microscopical examination.

Application of Reagents.—The exact method of inducing the reaction is, in fact, less important than the rigid and consistent standardization of conditions and their checking against a control analysis of the pure substance. In the case of many alkaloids too little is known concerning the optimum conditions of crystallization for chemico-microscopy, to lay down detailed rules of procedure. There are, however, certain general rules which must be observed.

First, in regard to the addition of reagents they must be added in as concentrated a form as possible. It is not generally desirable to add them solid unless it is certain that the quantity of solid material is less than will produce a supersaturated solution of the reagent in the drop of test solution. If the mixture becomes supersaturated with the reagent the test will be out of control and will have to be repeated. Saturated solutions of the reagents should normally be used.

Where the reaction is carried out on the microscopic slide, the reagent must not be added directly to the test drop. It should be deposited on the slide close to it. By means of a platinum wire or fine glass rod the reagent is then slowly and cautiously mixed with the test drop. A cover slip must not be applied until such time as it is judged that the crystallization is complete.

Secondly, one of the most serious contaminating influences is dust. It is essential that all operations should be carried out in an atmosphere which is free from dust.

Thirdly, both at the time of mixing reagent and test solution and throughout the reaction time the temperature must be carefully controlled. This can usually be done quite satisfactorily if the operations are carried out in a small room or cubicle which is maintained at a constant temperature. In special cases some form of thermostatic control may be necessary.

Subsidiary Processes.—There are some cases in which more satisfactory results are obtained if the reaction is carried out independently of the microscopic slide. This applies in particular to circumstances in which it is desirable to wash the crystals or recrystallize them. In some cases both these operations can be carried out upon the microscopic slide, but this medium is not always satisfactory.

Washing.—If the crystals are to be washed exactly the same procedure is followed as in capillary decantation. The reaction is carried out in a capillary of fairly wide bore. The crystalline precipitate is centrifuged down, the supernatant liquor is decanted, the residue washed with the appropriate solution, centrifuged and again decanted.

If the quantity of deposit is relatively large the tip of the capillary is filed off and the deposit expelled at that end direct upon the microscopic slide. If the deposit is small, the capillary should be filed off about 5 mm. from the bottom. The deposit can then be transferred with a platinum wire to the slide.

Recrystallization.—Recrystallization is a more complicated process and is difficult to undertake if the crystalline deposit is very small. It should not be attempted unless there is room for loss almost inevitably associated with recrystallization technique. The crystals are dissolved in a micro test tube in which the original operation was carried out. If the recrystallization is of the type in which the crystals can be redeposited from the hot solution on cooling, the matter is comparatively simple. If, however, concentration is necessary, it should be done with a current of warm air. The most satisfactory method is to attach to the test tube an outlet and inlet tube set in a stopper. The inlet tube is of sufficient length to allow of its being heated at a point remote from the test tube itself. The outlet tube is attached to a filter pump. The inlet tube is heated, not too strongly, and the filter pump run gently. Concentration can, of course, be carried out with direct heat, but it must be done very cautiously in a bath of appropriate temperature. As in decantation the deposit is centrifuged and the mother liquor removed.

The Chemico-Microscopical Identification of Alkaloids as Picrates.—Burt E. Nelson and Helen A. Leonard (*J. Amer. Chem. Soc.*, 1922, 369) describe a method for the micro-identification of picrates. These authors consider that the picrate derivatives give the most satisfactory results particularly where small quantities of the material are available. They stress the fact that a rigid control of the physical conditions is necessary. Among the most influential of these factors are temperature, concentration and purity of the material crystallized. They point out that minute traces of foreign substances such as grease upon the microscopic slide may seriously interfere with the reaction and lead to an incorrect interpretation of the results.

Method.—The aqueous solution of the separated alkaloid is made faintly acid with hydrochloric acid in a micro test tube. A saturated aqueous solution of picric acid is added. The precipitate formed is deposited centrifugally and washed by decantation several times. The residue is dissolved in a minimum quantity of 95% alcohol and the mixture is warmed on a water bath. This warm solution is allowed to cool slowly, the crystals separating on cooling. After this preliminary treatment more rapid cooling increases the yield. The mixture is then centrifuged, until the deposit is firmly packed. The supernatant liquor is poured off into a second micro test tube and preserved. A small portion of the crystalline deposit is now transferred to a paraffin ringed slide for microscopic examination.

The second tube containing the supernatant alcoholic liquor is now diluted with an equal volume of water. This alcohol-water mixture is now added to the remaining crystals of the first precipitation. The mixture is warmed until the deposit dissolves. On repeating the cooling, the crystals are redeposited.

By this means two microscopic preparations are obtained (1) crystallized from 95% alcohol and (2) from 50% alcohol.

These preparations are examined microscopically. The authors state that highly characteristic crystalline forms are produced in all cases, and that two preparations of the same alkaloid obtained under these different physical conditions serve in effect as a specific test for a given alkaloid. They supply no crystallographic data, but the crystalline formations are illustrated by means of drawings.

The importance of this technique is that it serves to show the need for the standardization of the conditions under which the test is carried out. Both heating and cooling must be controlled and the volumes of the solvents must be equal in all cases. Aerial contamination must be avoided since the deposition of minute quantities of dust will seriously interfere with crystallographic methods in general. It is also necessary to ensure absolute cleanliness of the microscopic slides. They should be treated first with hot alkali, washed, dried, and finally immersed in ether to remove every trace of grease. These precautions apply to all crystallographic determinations carried out on a micro scale. Serious errors of identification may result if the precautions are neglected.

The Chemico-Microscopical Identification of Alkaloids by other Methods.—There is a very large field for the development of this type of identification of alkaloids (and indeed other organic compounds) by chemico-microscopical methods.

Nelson and Leonard consider that picrates give the most characteristic crystalline forms in general but a similar technique can be applied using Marmé's reagent. It is satisfactory for the examination of small quantities because the method can be readily adapted to operations on the slide itself.

The best results with this reagent are obtained if Chamot's diffusion method (*p.* 26) is used. In place of decantation the separation of crystals from the mother liquor is effected by the mechanical method (*p.* 24). In our experience, as yet somewhat limited, the crystallographic characteristics of Marmé's addition products are less susceptible of interference by impurities than the picrates. This makes this form of preparation particularly suitable in those cases where the initial quantities of material are very small thus making elaborate manipulation impracticable.

The Chemico-Miscoscopical Identification of Synthetic Drugs. —G. Denigès (*Mikrochem.*, 1931, 9, 316–323) has described a method for the micro-chemical identification of synthetic drugs. The following are compounds whose micro-chemical reactions have been studied: veronal, soneryl, rutonal, luminal, dial, allyl-iso-propyl malonylurate, and allonal.

A small quantity of the material (less than a milligramme) is dissolved in ammonium hydroxide. This operation should be carried out on a microscopic slide which has been scrupulously cleaned, first by treatment with sodium hydroxide and, finally, after drying, with ether to remove the last traces of grease from the surface.

The ammoniacal mixture is now made slightly acid with sulphuric acid, 1 : 10. A cover slip then placed over the acidified drop and the preparation is examined microscopically with a magnification of about 60 diameters. Under these conditions most of the synthetic drugs form highly characteristic crystalline structures which are readily identified. Veronal forms rectangular plates either isolated or in groups. Soneryl forms long needles radiating from the centre. Rutonal produces regular hexagonal plates or groups of crystals which produce the appearance of foliage. Luminal forms rosettes. Dial is characterized by the formation of hexagonal plates and groups of rhomboids. Allyl-iso-propyl malonylurate forms elongated hexagonal plates.

Allonal is a compound of allyl-iso-propyl malonylurate with pyramidon. Under this treatment allonal forms the elongated hexagonal plates characteristic of allyl-iso-propyl malonylurate whilst with picric acid, yellow elongated prisms are formed which are characteristic of the pyramidon part of the molecule.

It will be noted that the crystalline forms observed after treatment by this method are highly characteristic and serve sharply to distinguish these synthetic drugs from each other. At the same time, dial and rutonal, both of which form hexagonal plates, may in some circumstances be confused.

Rutonal is, however, a phenyl derivative whilst dial is not. If a drop of 2% sulphuric acid is added to the material to be tested on a microscopic slide and the mixture is gently warmed, phenyl-substituted compounds such as rutonal and luminal give an intense brown coloration and yield a precipitate on dilution. Non-phenyl derivatives such as dial give a red-brown colour.

If proper precautions are taken in carrying out this test the results are reliable. The same care must, however, be taken to control the conditions of temperature and concentration, as in the case of the micro-chemical identification of alkaloids. Aerial contamination must be avoided as in all other cases where micro-chemical tests of a crystallographic type are being carried out.

As with the crystallographic detection of alkaloids it is advisable to use the mechanical method of separation of crystals from liquor (*supra*). In general it is important to observe that the manner in which the reagent is brought into contact with the test solution is of major importance in crystallographic operations. This is especially true where the concentration of the material sought is feeble. Very cautious agitation of the mixture is in all cases desirable. The diffusion of the reagent into the solution to be tested is the best general method, and it is usually advisable to avoid any elaborate manipulation of the crystallizing material. Subsidiary operations such as centrifuging should be avoided if possible, and it is preferable when practicable to carry the whole operation out on the microscopic slide.

As in the case of alkaloids any contamination with dust must be carefully guarded against. The control of temperature is less important than in the case of the tests for alkaloids, but it cannot be neglected. It is safer to maintain a constant temperature during the reaction.

The concentration of acid must be carefully controlled and constant. The sulphuric acid drop should be of the same volume in all cases, and should not exceed that of the test solution in volume. This is ensured by placing the drops side by side and using the same capillary pipette (30 to 40 drops per cc.) as that employed for the previous operations.

(b) The Detection of Abortifacients

The detection of so-called abortifacient drugs is an important part of the chemico-legal practice. We are not here concerned with the fact that the majority of the substances reported to be abortifacients are not so in fact and that their sale is not only a danger to the public but constitutes a sort of fraud upon the victims who purchase them. But they are, in fact, poisons or at least "noxious things," their administration may result in death, and their use is criminal.

The following substances are very commonly used as abortifacients: Ergot, Savin, Pennyroyal, Tansy, Apiol, Cantharides, Absinthe, Artemisia (Mugwort), Rue, Aloes, Taxus baccata (Yew), Gamboge. Not all these substances are amenable to chemical identification but at our laboratories at Lyon a number of empirical tests have been devised which in many cases serve to identify them. These tests are in general applicable on a micro-scale, and the methods already described for the preliminary preparation of the material are applicable to the examination. The tests themselves, however, vary a great deal in sensitivity, and they are not in all cases capable of identifying minute quantities of the substances sought, and some of the tests are clearly not practicable on anything less than a semi-micro scale. They have, however, been included because they have not previously been described in any hand- or text-book of forensic chemistry. If the limitations of these tests are kept in mind, they are of great use under favourable conditions.

(1) **Ergot.**– Since it acts selectively upon the uterus this substance can be classified as a true abortifacient. The active principle of this fungus is ergotinine $C_{34}H_{40}N_4O_6$ (*Fauret*) $C_{35}H_{41}N_5O_6$ (*Fr. Codex Supp.*), and ergotamine $C_{35}H_{39}O_5N_5$ (*Barger and Carr*).

Being an alkaloid it can be extracted by the methods described. If a portion of the extract is made alkaline with potassium hydroxide and heated, trimethylamine is produced and detected by its characteristic smell. Sulphuric acid 1 : 7 produces a red-violet colour, changing to blue. In ethereal solution the addition of crystals of oxalic acid produce a red colour.

(2) **Savin.**—This oil contains a terpene $C_{10}H_{16}$ known as sabinene. It is dangerously toxic producing gastro-enteritis and tetanic spasms.

The following tests are characteristic. Mixed with an equal volume of chloroform and after the addition of sulphuric acid, the acid and chloroform layers separate. The acid layer becomes blood red in the presence of sabinene. Hydrochloric acid in alcohol gives pale red and then violet, sulphuric acid, orange-brown. Fröhde's reagent, red-brown. Iron perchlorate in sulphuric acid (a slow reaction) cherry-red.

(3) **Gamboge.**—Gamboge is a yellow resin, which can be separated from such oils as apiol and savin by steam distillation. It remains as a residue in the form of a yellow emulsion. If this emulsion cannot be filtered clear and retains its yellow colour the resin is present. This test distinguishes it from aloes, which leaves a residue after distillation which is also yellow in colour. The solution can, however, be filtered clear. A yellow precipitate forms in the filtrate on the addition of potassium hydrate and lead acetate.

(4) **Aloes.**—Besides the tests described the active principle, aloetine, can be identified by the following reactions. In benzene solution aloetine produces a red colour when shaken with potassium hydroxide solution or ammonia. In aqueous solution aloines give a blue-black coloration with ferric chloride in the cold (*Guillemard*). Heated with a drop of

copper sulphate solution and 1 or 2 cc. of hydrogen peroxide aloine gives a strawberry-red coloration.

(5) **Absinthe.**—The active principle of absinthe is santonin, a crystalline substance composed of four-sided flat prisms which are white or faintly yellow. If santonin is dissolved in strong sulphuric acid, and the mixture is warmed and ferric chloride added a red colour changing to purple is produced.

(6) **Mugwort (Artemisia).**—Although quite ineffective as an abortifacient the decoction is frequently taken to induce abortion, Jacques Locard (*Laboratoire de Police Technique, Lyon*), states that the following tests serve to identify mugwort. (1) Ferrous sulphate produces a dark green precipitate. (2) Potassium bichromate produces a coloration resembling tincture of iodine. (3) An abundant precipitate slow in formation is produced with silver nitrate. (4) Strong acids produce a dark coloured precipitate.

(7) **Rue.**—Sulphuric acid gives a very dark red-brown coloration which assumes a chocolate colour on the addition of alcohol. Nitric acid gives a dark cherry-red.

(8) **Apiol.**—This substance is the active principle of parsley.

A method for the identification of apiol was devised by Guillemard working in our laboratories at Lyon. A few drops of Millon's reagent are added to the material to be tested. On shaking, a very intense red colour is produced. Alternatively, a few drops of the material are extracted with carbon disulphide. Bromine sulphocarbonate is then added until the coloration persists. On evaporation, crystals of tribrom-apiol are deposited which can be recrystallized from absolute alcohol in the form of white needles melting at 80° to 90° C.

Tansy, cantharides, and yew are not readily identified by chemical methods.

The Stas-Otto principle already described is, in general, applicable for the isolation of these substances from the stomach or viscera. It will have been noted that the majority of these substances are either alkaloidal or they are volatile oils, or resins. The volatile oils pass over when the material is steam distilled while the resins remain behind. Substances of an alkaloidal nature can be extracted with alcohol and subsequently with acidulated water in the manner described.

THE MICRO-CHEMICAL DETECTION OF ARSENIC

Arsenic is so frequently encountered in forensic practice that a special discussion of its detection and estimation is desirable. Dusts, stains, deposits from utensils, the gome from fingernails, deposits in the ears or respiratory passages may, if arsenic is discovered in them, provide valuable evidence in criminal and civil cases.

Since the classical methods themselves are of a micro or semi-microchemical character their consideration here is appropriate. But in forensic cases, and particularly in the preliminary stages of an investigation involving arsenic which has been submitted to a police laboratory, alternative methods of detection and estimation may prove more convenient. The classical methods for the estimation of arsenic are not, strictly speaking, micro-methods because initially they are designed to deal with macro quantities of the sample even if the arsenic is present in micro amounts. The situation may be, and frequently is, quite different in the special conditions described above. The quantity of the initial sample may be of the order of milligrammes. If this is the case and if the traces of arsenic only are present the classical methods are not applicable.

As Arsine.—Chamot (*Handbook of Chemical Microscopy, Vol. II, p.* 223) describes an elegant apparatus for the detection of traces of arsenic as arsine. The test is, in effect, a micro modification of the Gutzeit reaction in its classical form using silver nitrate as indicator. It consists (1) of a gas generator with a neck to introduce the reagents. It terminates in an absorption chamber. (2) A separate unit consisting of a capillary tube with a wide end of the same diameter as the absorption chamber to which it is attached by means of a piece of rubber tubing.

The procedure is as follows: A small fragment of silver nitrate is first introduced into the capillary and secondly a particle of lead acetate of somewhat larger size. This should be separated from the silver nitrate by a distance of about five millimetres.

Arsenic free zinc is introduced into the lower limb of the gas generator and dilute arsenic free HCl into the upper limb. The generator neck is then stoppered with a wooden plug which prevents the running back of the acid into the lower limb. A plug of cotton wool soaked in lead acetate and dried is then inserted into the absorption chamber in such a way that it does not come in contact with the acid. The capillary is then attached to the absorption chamber and gas generator.

The stopper is removed which allows the acid to be run back into the lower limb of the generator. The stopper is then replaced after the neck has been slightly moistened to swell the wood and seal the joint.

As the hydrogen evolves and fills the apparatus the crystal of silver nitrate is closely watched with a powerful hand lens or under the microscope with a low power. If the silver nitrate does not change colour the materials are free from arsenic.

The stopper is again removed. The material to be tested in hydrochloric acid solution is introduced into the lower limb as quickly as possible and the stopper replaced. A drop of water should be placed at the juncture of the stopper and neck to ensure the proper resealing of the joint.

The silver nitrate crystal is again observed with the lens. If arsenic is present, the crystal first becomes yellow and finally black. The crystal of lead acetate must also be closely observed at the same time. If this shows any darkening it indicates that any hydrogen sulphide evolved has not been completely absorbed by the absorption plug and is passing over into the capillary. Incomplete absorption of the H_2S of course invalidates the test.

This is a very delicate test for arsenic, but it is not absolutely specific. Antimony gives the same secondary reaction with silver nitrate. Stibine does not, however, form any primary complex equivalent to the hypothetical $AgNO_3Ag_3As$ to which the first yellow coloration is said to be due. Thus, if the silver nitrate crystal passes from yellow to black it is generally safe to assume the presence of arsenic.

By Chemico-Microscopy.—In our experience, chemico-microscopical tests are not very satisfactory for the detection of arsenic in dust and related materials. The reason for this appears to be that the technique for preparation of the material profoundly influences the crystallographic effects, and in dealing with materials of so variable a character as dusts, variations in technique are inevitable.

In regard to preliminary preparation of the sample, however, it has been found that Stryzowski's method is the most satisfactory for general application. It has the advantage of being readily adapted on a micro-scale. The sample is treated with a drop of a saturated solution of magnesium nitrate made alkaline with magnesium oxide. The mixture is charred and finally ashed in the micro-muffle. The cooled ash which if arsenic is present contains magnesium pyro-arsenate is taken up with hydrochloric acid. Silica, very frequently present in dusts, is a source of gross interference with the crystallographic reaction and must be completely separated. The hydrochloric acid solution is accordingly evaporated to dryness and the residue gently baked. It is then again taken up with hydrochloric acid and filtered by the capillary method.

Short's method described by Chamot (*loc. cit.*, *p.* 226) to form the complex $(NH_4)_3AsO_4 12MoO_3 nH_2O$ can then be followed. Under optimum conditions the octahedra and cubes formed characteristic of the ammonium arsenate molybdate complex are readily identified. The presence of magnesium due to the preliminary treatment does not interfere. Short's method also inhibits crystallographic formations due to other radicles which might be confused with those of arsenic.

At the same time it is desirable, wherever possible, to confirm the presence of arsenic by an alternative method.

The Reinsch Test.—This method is capable of adaptation on a micro-scale. The material should be prepared by Stryzowski's method and the residue taken up in very dilute arsenic free HCl. It is filtered by the capillary method and the same capillary (1·5 to 2 mm. diam.) should be used for the test. This is done by sealing off the free end of the capillary and shaking or centrifuging the solution down.

A piece of arsenic-free copper wire 0·2 to 0·3 mm. in diameter is suitable for the test. A blank test is carried out in the following manner. The arsenic free HCl of the same concentration as that used to dissolve the sample is placed in a micro test tube with a few drops of a dilute solution of ferric chloride. A piece of copper wire is introduced of sufficient length for a portion of it to be free of the level of the liquid. For convenience in handling it may be of the same length as the test tube.

The solution is then boiled for three or four minutes, water being added when necessary to maintain the original volume.

The copper wire is then withdrawn, washed and dried. An examination either with a high power lens or under the microscope with a low power objective is then made. This should be done at the point of juncture corresponding with the level of the test solution in contact with the copper wire so that the appearance of the treated and untreated section can be compared. If no trace of deposit is observed in the treated portion, the materials are arsenic free.

A length of the same copper wire is then introduced into the capillary. This must be heated by means of a bath boiling at a temperature a little in excess of 100°C. The boiling must be continued for 15 minutes in the first place and the volume maintained by the addition of water from a capillary of small bore. The copper wire is then washed, dried and examined with a lens or microscope as before. A grey deposit indicates the presence of arsenic. If, however, the test is negative on the first boiling, the process should be repeated for a further 15 minutes.

Because antimony, bismuth, gold, mercury, platinum, silver and tin are also deposited upon copper by this method, the nature of the deposit must be crystallographically confirmed, by examination of the sublimate. The wire carrying the deposit is placed in a scrupulously clean dry capillary. This is gently heated and the sublimate examined on the microscope stage with a low power. The sublimed As_2O_3. forms brilliant octahedra of highly characteristic appearance.

If the quantity of the sample permits, all three tests for the detection of arsenic should be utilized. If two only are practicable, the arsine and Reinch tests should be applied. If a single test must suffice, the arsine method should be used.

THE MICRO-CHEMICAL ESTIMATION OF ARSENIC

In the case of dusts and related materials it may occasionally be important quantitatively to estimate the arsenic contained in them. Some discussion of quantitative methods thus appears desirable.

Strictly speaking, the March and Gutzeit methods are semi-micro operations since macro quantities of the sample itself are generally involved in the estimation, but since they are applicable to comparatively small quantities of material, they will be considered.

Micro-Chemical Method (Modified by Preghl).—This relies upon the oxidation of the arsenic to arsenic acid and its precipitation as magnesium ammonium arsenate. It is a classical method originally adapted by Aberhalden (*Handbuch der Biochemischen Arbeitsmethoden*, 1919).

Quantities of the order of 5 mgm. are sufficient for this estimation. The oxidation of the arsenic is carried out in a capillary open at both ends into which the material is weighed. The capillary is placed in a reaction tube of hard glass about 19 mm. in external diameter. 0·5 to 1 cc. of nitric acid is introduced into the reaction tube containing the capillary. The reaction tube is then sealed at the upper end and the whole is heated in a micro muffle for some time at 250 to 300°C. until the material is completely oxidized.

The procedure is then as in the classical method making use of miniature apparatus. The precipitate is filtered through a micro-Neubauer crucible described by Preghl, ignited and weighed as magnesium pyroarsenate.

Because of the simplicity of the preliminary method of treatment, this process is particularly suitable for the treatment of small quantities of dust. Being carried out in a sealed tube preliminary chances of loss are eliminated. It is usually recommended that the acid in the reaction tube be transferred to a dish for evaporation before taking up in ammonia and precipitating. But if a hard glass tube properly rounded in sealing at the lower end is used, it can frequently be utilized for the evaporation, the taking up in ammonia, and the precipitation itself. It is necessary only to file off the upper sealed end, wash and remove the capillary, and utilize what is then, in effect, a rather wide micro-test tube. This is not very convenient for evaporation, but a troublesome transference is saved and the volume to be evaporated in consequence remains small, and can thus be evaporated in the tube without undue trouble. Another advantage of precipitation in the ignition tube is that the precipitate can be washed by decantation with centrifuging. This greatly reduces the filtration difficulties which can arise with magnesium ammonium arsenate.

CLASSICAL MICRO-CHEMICAL METHODS

The Gutzeit Test.—The Gutzeit test relies essentially upon the same principle as the classical Marsh-Berzelius test. It has the advantage of being rapid and simple, and as recently modified it is quantitatively accurate. The classical form of the test was to produce arsine by the generation of hydrogen in the presence of the arseniferous material and to bring it into contact with bibulous paper, moistened with silver nitrate. A black stain was produced. Silver nitrate is, however, unsuitable by reason of its sensitiveness to other agents such as light and traces of hydrogen sulphide. Mercuric chloride has now replaced silver nitrate as a detector. This salt is, of course, also affected by hydrogen sulphide, but it is much less sensitive than silver salts. On the other hand, it is extremely sensitive to the presence of traces of arsenic, producing with it a yellow stain, which passes through lemon-yellow, bright yellow, orange to orange-brown, according to the amount of arsenic present. The test is more sensitive than the Marsh test and when sulphides are removed it is extremely satisfactory either for the detection or estimation of traces of arsenic.

Dowzard (*J. Chem. Soc.*, *lxxix*, *lxxx*, 463, 715) has devised a method of efficiently washing the gas. It consists of a superimposed series of glass cells, the lowest of which fits the neck of an Erlenmeyer flask. These cells are filled with lead acetate and cuprous chloride in hydrochloric acid and are so constructed that the generated gas bubbles through the solution before it escapes. By this double washing, phosphoretted hydrogen and hydrogen sulphide both of which react with mercuric chloride are removed.

The test does not require elaborate manipulation. A weighed portion of the sample is mixed with 5 cc. of pure arsenic-free hydrochloric acid, four drops of a 15% solution of cuprous chloride are added, and the volume made up to 30 cc. with water. The volume may be increased but the concentration of acid must be constant. A rod of arsenic-free zinc is placed in the flask and the mixture added. The cells containing the lead acetate and cuprous chloride are placed in position and the bibulous paper moistened with mercuric chloride adjusted over the mouth of the the exit tube. If after forty minutes no stain is observed, no arsenic is present. Light yellow stains indicate minute traces, orange-brown, heavy traces.

Standards can be prepared in the same manner, using a solution containing known quantities of arsenic.

The Marsh-Berzelius Test.—Despite refinement in the technique of the Gutzeit test which makes it available for quantitative determination, it is still generally used only as a sorting test. Officially, the Marsh-Berzelius test is still employed for all quantitative determinations of traces. The principle of the test is well known as depending upon the reduction of compounds of arsenic and antimony to produce arsine and stibine respectively by nascent hydrogen in an apparatus which consists of a hydrogen generator, a calcium chloride tube to dry the evolved gas and a capillary in which the arsenic is sublimed. This is cooled by a drip-flow of water.

Evolution of Hydrogen.—Three different methods are used for the evolution of hydrogen. The Joint Committee of the Societies of Chemical Industry and of Public Analysts (*Analyst*, 27, 1902), (*J.C.S.I.*, 21, 1902), recommend an apparatus in which the hydrogen is generated from pure zinc and sulphuric acid. The second method is the electrolytic in which a dilute solution of sulphuric acid is electrolysed between platinum electrodes. The third method which is not commonly used is one in which the hydrogen is generated independently.

The first of these methods is the simplest but it depends upon the absolute purity of the zinc whereas the electrolysis between platinum electrodes eliminates this requirement. There is, however, an electrolytic method which we have used at Lyon in which the anode is of platinum and the kathode of pure zinc. The advantage of this method is that the arsine is liberated with great readiness and completeness even from zinc which is defective in " sensitiveness " (*vide infra*). The disadvantage is that zinc must be used which is one of the objects of the electrolytic method to avoid.

THE REAGENTS

Zinc.—Lack of " sensitiveness " in the zinc means that despite its ready reaction with acid which is common to all zinc the gas evolved by the metal will not always release the arsenic from the test solution. The cause of this interesting phenomenon is not understood. It was found by Chapman (*Analyst*, 32, 1907, 247–9) that if the zinc is coated with cadmium it becomes sensitive. It is, however, essential that the cadmium coating should be uniform. Cadmium being below zinc in the electro-chemical series is deposited upon it if zinc is placed in a solution of a cadmium salt. In practice, 25 grams of pure granulated zinc are treated with dilute nitric acid and then quickly washed. The zinc is then placed in a flask with 50 cc. of a 4% solution of cadmium sulphate or chloride. The mixture then stands with occasional shaking on a water bath until the spongy deposit of cadmium covers the zinc. The couple is finally washed.

A control test is made with a solution containing 0·01 mgm. of arsenious oxide. A distinct mirror should be formed. If the zinc is still found to be insensitive the cadmium coating is increased. If the zinc still remains insensitive it should be rejected and a fresh sample chosen.

If the zinc is used in connection with the electrolytic process we have not found it so liable to insensitiveness. Some workers have questioned the utility of cadmium treatment of the zinc rod. They consider that if the zinc is insensitive in the electrolytic process it must be rejected. No final conclusion upon this point can be offered.

Sulphuric Acid.—Arsenic is a common impurity of this acid, but it is now always possible to secure an arsenic-free supply. The acid can, however, be purified by distillation over pure sodium chloride (*Royal Comm. on Arsenical Poisoning*, 2.206). Since most bottle-glass contains traces of arsenic it must not be stored for long in bottles.

Calcium Chloride.—This salt often contains heavy traces of arsenic, but it is now commonly supplied arsenic free. It can be purified by moistening with pure hydrochloric acid fusing and regranulating. It has been stated that under certain conditions which have not been defined, calcium chloride absorbs arsine (*Dyer*).

Glass Wool.—Cotton wool should on no account be used to plug the calcium chloride tubes. Ward has shown (*Analyst* 51 (1926), 457) that cellulose will in certain conditions absorb arsenic. Glass wool should always be used to plug the tubes.

Interfering Substances.—The following metals in the form of salts interfere with the evolution of arsine: iron, platinum, copper, nickel, and cobalt.

Oxidizing agents are, of course, destructive of the gas. Thus potassium chlorate, chlorine, bromine, nitrates, and nitric acid must not be present. Reducing agents such as stannous chloride (which is the most satisfactory), sodium sulphite, or potassium metabisulphite may be used for reduction. Excess of stannous chloride must be avoided, since tin, although unobjectionable in small quantities, is said to interfere if in excess.

Blank Experiments.—It is essential that blank experiments be carried out on all reagents and a final test using the reagents together as in the test itself should be made. After every precaution has been taken there is a tendency for the reagent to absorb arsenic from surrounding materials or from the atmosphere. Blank experiments must therefore be carried out periodically. It is also essential to guard against the apparatus itself absorbing arsenic in the region of the calcium chloride tube. If, for example, the apparatus consistently produces absolutely clean blanks, it should be thoroughly overhauled, since it may be an indication that absorption is taking place within the apparatus.

Standard Mirrors.—Mirrors should be prepared from a standard solution of pure arsenious oxide in hydrochloric or sulphuric acid equivalent to 0·001 mgm. of As_2O_3 per cc. In our experience sulphuric acid is more suitable. A series of mirrors is prepared, equivalent to 0·002 mgm. to 0·2 mgm., each increasing by 0·002 mgm. Comparison is not possible with quantities in excess of 0·2 mgm.

It is very important that the tubes should be uniform at the point where the mirror is deposited. This uniformity can be assured by the use of a copper rod which is pushed into the capillary until it engages with the walls. A mark is then made at this point with a grease pencil. When the test is made the filter paper which is placed on the tube to distribute the water for cooling is so arranged as to correspond with the pencil mark. This ensures that the sublimed arsenic will be deposited in the tubes at points where the bore is uniform. The importance of this cannot be exaggerated. If mirrors, which are quantitatively equal, are distributed upon a different area, it is obvious that their density will vary. Since the comparative test is, in fact, a comparison of density, serious errors will arise if the area of the tubes at the point where the deposition occurs is a variable.

Micro-Gravimetric and Volumetric Methods.—The method of comparison has been shown to be such as to distinguish between mirrors differing by quantities of the order of 0·002 mgm. It is, however, possible to utilize the micro-balance for the purpose of weighing the deposit. This is, of course, strictly a sounder method providing a micro-balance of sufficient accuracy is available.

In practice, however, the micro-volumetric method is more satisfactory. The mirror is dissolved in 0·005 N iodine containing a little sodium bicarbonate. The solution is then made faintly acid with HCl and titrated back with sodium thiosulphate using starch as indicator. A micro-burette graduated in 0·002 cc. must be used. In all cases these methods should be used as a check against the method of comparison with standard mirrors.

REFERENCES

Alten and Knippenberg . . . (*Detection of Ca*), Biochem. Z., 1933, 265, 85.

Ames . . . *Ames on Forgery*, New York, 1900.

Behrens . . . *Manual of Microchemical Analysis*, London, 1894.

Beroud . . . *L'expertise des faux en ecriture par alteration*, Lyon, 1923.

,, . . . *Un cas d'empoisonnement par la veratrine*, Rev. Inter. de Crim,. 1933, 239.

Bischoff . . . *Die chemische Untersuchung der Tinten.*

Blackburn and Cadell . . . *The Detection of Forgery*, London, 1909.

Brewster . . . *Contested Documents and Forgeries*, Calcutta, 1932.

Brouardel . . . *Les Explosifs et les Explosions*, Paris, 1897.

Brunck . . . (*Detection of Ni*), Z. angew. Chem., 1907, 20, 834.

Buchwald . . . *Bleistifte Farbige Kreiden und Pastelstifte*, Leipzig, 1904.

Bieger and Diesselhorst . . . (*Chlorides in Sweat*), Deut. Med. Wochschr., 29, 1903.

Burrard . . . *The Identification of Firearms and Forensic Ballistics*, London, 1934.

Carrel . . . *Contribution a l'Identification des encres en criminalistique*, Lyon, 1943.

Carvalho . . . *Forty Centuries of Ink*, New York, 1904.

Cazaneuve . . . (*Detection of Hg*), C.r., 1900, 131, 346.

,, . . . (*Detection of Cd*), C.r., 1900, 131, 346.

Chamot and Mason *Handbook of Chemical Microscopy*, London, 1940

Chiarottino . . . (*Detection of Co*), L'indus Chim , 1933, 8, 32.

Claps . . . *Identification of Lip Impressions*, Rev. Inter. de Crim., 1931, 707.

Cross and Bevan . *A Text Book of Paper-Making*, London, 1907.

Dennstedt . . . *Die Chemie in der Rechtsflege*, Leipzig, 1910.

Dennstedt und Voightlander . *Lehrbuch der gerlichtlichen Chemie*, Brunswick, 1906.

De Rechter et Tihon *L'evolution de l'expertise en ecriture*, Bruxelles, 1922.

Edgeworth-Johnstone *J S.C.* 1. 50 182 T. 1931.

Eruich . . . *Lehrbuch der Mikrochemie*, München, 1926.

,, . . . *Mikrochemisches Praktikum*, Leipzig, 1931.

,, . . . (*Micro-chemical Practice*), Analyst, 1931, 56, 138.

Evans . . . *Counterfeit Coins and Notes*, Police Jour., 7, 1934, 456.

Feigl . . . (*Detection of Ba and Sr*), Mikrochem, 1924, 2, 188.

,, . . . *Qualitative Analyse mit Hilfe von Tüpfelreaktionen*, Leipzig, 1931.

,, . . . (*Identification of Al*), Mikrochem, 1923, 1, 17.

,, . . . (*Determination of Cu*), Ber., 1923, 56, 2083.

,, . . . (*Determination of Fe* (*ous*)2, Z. Anal, Chem., 1932, 90, 199.

Feigl and Neuber . (*Detection of Bi*), Z. Anal. Chem., 1923, 62, 273.

Feigl and Stern . (*Identification of Al*), Z. Anal. Chem., 1921, 60, 9.

Finn and Cornish . *Development of Fingerprints*, Ind. Eng. Chem., News Ed., 1935, 73, 75.

Fleury et Silvera . *Determination de la date d'usage des armes à feu.*

Forgeot . . . *Les Empreintes Digitales etudiée de Point de Vue medico judicaire*, Lyon, 1891.

,, . . . *Les Empreintes latentes*, Lyon, 1891.

FOYATIER . . . *Etude sur les réaction des composés nitrée des poudres*, Ann. de Med. leg., 10, 1924.

FRAZER . . . *Des faux en critures et de l'ecriture*, Paris, 1899.

" . . . *Bibliotics or the Study of Documents*, Philadelphia, 1901

GAND . . . *L'expertise des taches de sang*, Rev. Inter. de Crim., 1931, 38.

GIBLIN . . . (*Detection of Ba and Sr*), Analyst, 1933, 58, 752.

GLAISTER . . *Medical Jurisprudence and Toxicology*, Edinburgh, 1938.

GOUILLON . . *Traité methodique de la Fabrication des Encres*, Paris, 1906.

GREY . . . *Practical Chemistry by Micro-Methods*, Cambridge, 1925.

GRIFFIN AND LITTLE *Chemistry of Paper-Making*, New York.

GROP AND HOPLER . *Handbuch fur Untersuchungsrichter*, Berlin, 1922.

GROSS . . . *Criminal Investigation*, London, 1934.

GUARESCHI . . *Gli Inchiostri da Scrivere*, Milan, 1915.

GUTZEIT . . . (*Detection of Sn*), Helv. Chim. Acta., 1929, 12, 720.

GUILLEMARD . . *Sur la determination de quelques substances dites abortives*, Arch. Anthr. Crim., Sept., 1914.

GUIRAL . . . *La valeur de la preuve dans l'expertise des ecritures*, Thèse de Lyon, 1927.

HALLER AND GIRARD *Memento du Chimiste*, Paris, 1919.

HARDER-BRUNNING . *Die Kriminalität bei der Post*, Berlin, 1924.

HENRY . . . *The Plant Alkaloids*, London, 1924.

HERZBERG . . *Papierprüfung*, Leipzig, 1915.

HILL . . . (*Determination of Fe (ous*), Proc. Roy. Soc., 1930, 107, B. 205.

HUSSON . . . *De la detection et l'identification des taches de sperme*, Rev. Inter. de Crim., 1934, 407.

ICARD . . . *Le cerumen au point de vue medico-légal*, Annales d'hygiene publique, Juin, 1921.

JESERICH . . . *Chemie und Photographie im Dienste vor Verbrechersaufklarung*, ——, 1933.

JONES . . . (*Determination of Ni*), Analyst, 1929, 54, 582.

KERSTING . . (*Detection of Nitrates*), Annalen, 1863, 125, 254.

KING . . . *Analyst*, 1933, 58 325.

KNORRE . . . (*Determination of W*), Ber., 1905, 38, 783.

KOMAROWSKY AND POLNEKTOFF . . (*Detection of Boric acid*), Mikrochem., 1933–34, 14, 317.

KRATTER . . *Lehrbuch der gerichtlichen Medizin*, Stuttgart, 1927.

LACASSAGNE ET MARTIN . . *Précis de Medecine légal*, Paris, 1921.

LAMPITT AND SYLVESTER . . (*Determination of Al*), Analyst, 1932, 57, 418.

LATTES . . . *Die Individualität des Blutes*, Berlin, 1925.

LECHA-MARZO . . *Nuevos reactivos para la revelacion de huellas digitales invisibles*, La Policia cientifica enero, 1914.

LEHNER . . . *Ink Manufacture*, London, 1902.

LEUNG . . . (*Analysis of Sweat*), Thése de Lyon, 1931.

" . . . *Determination de l'origine du sang par les cristaux de Stryzowski*, Rev. Inter. de Crim., 1931, 738.

LEWIN . . . *Traité de toxicologie*, Paris, 1907.

LEWIS . . . *Spectroscopic Analysis*, Analyst, 60, 1935, 10–17.

LOCARD . . . *La Determination des taches de sang par le bromure de sodium*, Rev. Inter. de Crim., 1934, 92.

Locard . . . *L'analyse des poussières en Criminalistique*, Rev. Inter. de Crim., Sept., 1929, 176.

,, . . . *Manuel de Technique policière*, Paris, 1923.

,, . . . *Traité de Criminalistique*, Lyon, 1933–1936.

Loock . . . *Chemie und Photographie bei Kriminalforsuchungen*, Düsseldorf.

Lucas . . . *Forensic Chemistry*, London, 1935.

Lynch,—Roche, Slater and Osler (*Isolation of Pb*), Analyst, 1934, 59, 787.

Marshall . . *Explosives*, London, 1917.

Martini . . (*Identification of Co, Fe, Zn*), Mikrochem., 1930, 8, 144.

Majer . . . (*Detection of Hg*), Z. Anal. Chem., 1932, 87, 352.

Mayer . . . *Die gerichliche Schriftuntersuchung*, Berlin, 1933.

Medinger . . *Contribution au diagnostic de traces minimes de sang*, Rev. Inter. de Crim., 1931, 493.

Minovici . . *Manuel technic de medicina legala*, Bucharest, 1904.

Mitchell . . *Documents and their Scientific Examination*, London, 1922.

,, . . *The Examination of the Age of Ink in Writing*, Analyst, 45, 1920.

,, . . *Copying Ink Pencils and an Examination of their Pigments in Writing*, Analyst, 42, 19, 17.

,, . . . *The Deciphering of Scorched Documents*, Discovery, 5, 1924, 336–9.

Mitchell and Hepworth . . *Inks*, London, 1924.

Mitchell . . *The Detection of Fingerprints on Documents*, Analyst, 45, 1920, 122–9.

,, . . *Blacklead Pencils and their Pigments in Writing*, Jour. Soc. Chem. Ind., 1919, XXXVIII, 138, I.

,, . . *Science and the Criminal*, London, 1911.

Mitchell and Prideaux . . *Fibres used in Textile and Allied Industries*, London, 1910.

Mitchell and Ward *Sediments in Ink and Writing*, Analyst, 1932, 760.

Metzger, Rall and Heess . . *Urkundenfälschung*, Archiv. fur Kriminologie, Bd., 89, 5 u. 6, 1931, 197.

Müller . . (*Determination of Fe* (*ous*), Mickrochem., 1933, 12, 307.

Naudin . . . *L'enquete criminelle*, Paris, 1927.

Osborn . . . *Questioned Documents*, New York, 1929.

Pass and Ward . (*Detection of Cd*), Analyst, 1933, 58, 667.

Pavelka . . . (*Detection of Pb*), Mikrochem., 1929, 7, 303.

Pittius, van . . *Corrosion of Firearms*, Zeitsch. angew. Chem., 1906.

Pollard . . . *Automatic Pistols*, London, 1920.

Poluektoff . . (*Detection of K*), Mikrochem., 1933, 34, 14, 265.

Poore . . . *A Treatise on Medical Jurisprudence*, London, 1901.

Popp . . . (*Examination of Bombs*), Chem. Zeit., 1910, 1080.

,, . . . *Die Mikroscopie im Dienst der Kriminaluntersuchung*, Archiv. für Kriminologie, 70 Bd., 1918.

,, . . . *Fixierung von mit Iod* (*Fingerspuren*), Rev. Inter. de Crim., 1929, 492.

Pregl . . . *Quantitative Organic Micro-analysis*, London, 1924.

Quirke . . . *Forged Anonymous and Suspect Documents*, London, 1930.

RAMMSTEDT . . . *Tinte und Tusche*, Stuttgart, 1932.

REISS . . . *Manuel de police scientifique*, Lausanne, 1911.

RHODES . . . *Science and the Police Officer*, London, 1935.

RHODES . . . *Forensic Chemistry*, Man. Chem., VIII, 9, 287.

,, . . . *Development of Fingerprints*, Rev. Inter. de Crim., 1933, 328.

,, . . . *The Scientific Examination of an Historic Document*, Chem. and Ind. 50, 15, 303.

RHODES . . . *The Oxidation of Ferrous Iron in Iron Gall Inks*, Chem, and Ind, 59, 9, 143.

RUNGE . . . *Grundriss dea Chemie*, ——, 1847.

SCHLUTTIG AND NEUMANN . . *Die Eisengallustinten*, Dresden, 1890.

SCHNEICKERT . . *Kriminalistische Spurensicherung*, Berlin, 1925.

SCOTT . . . *Standard Methods of Chemical Analysis*, London, 1926.

SHORE . . . *Crime and its Detection*, London, 1931.

SMITH . . . *Taylor's Principles and Practice of Medical Jurisprudence*, London, 1920.

SMITH, SYDNEY . *The Identification of Firearms and Projectiles*, Police Journal, I, 1928, 419.

SÖDERMAN . . *Un appareil nouveau pour recueillir par aspiration les poussières*, Rev. Inter. de Crim., 1931, 373.

,, . . *Contribution à la technique de l'analyse des poussières en criminalistique*, Rev. Inter. de Crim , 1932, 486.

SÖDERMANN OCH FOUTELL . . *Handbok i Kriminaltetsick*, Stockholm, 1930.

SÖDERMANN . . *L'Expertise des Armes à Feu courtes*, Lyon, 1928.

SOLARO . . . *Studio Microscopico e Chemico pel Reconoscimento delle Fibre vegetali*, Milan, 1914.

SOMMER AND PINEAS (*Detection of Nitrates*), Ber., 1916, 48, 1963.

STEPHENSON . . *Some Micro-chemical Tests for Alkaloids*, London, 1921.

STIRLING . . . *Identification of Palmar Surface*, Rev. Inter. de Crim., 1921.

STOCKIS . . . *Development of Fingerprints*, Arch. Inst. de med. leg. aout, 1912.

STOVER . . . (*Determination of Cr*), J. Amer. Chem. Soc., 1928 50, 2363. ,

SYMONS . . . *The Evidence of Gun Wads*, The Police Jour., 6, 1933, 103–19.

TAYLOR AND WALLS *Nature*, 3727, 1941.

TÜRKEL . . . *Atlas der Bleistiftschrift*, Graz, 1927.

VUILLEMIN . . *Des Poussières au point de vue medico-legal*, Thèse de Nancy, 1926.

WAR OFFICE . . *Text Book of Small Arms*, 1929.

WEBSTER . . *Legal Medicine and Toxicology*, Philadelphia, 1930.

WILKINS, WOLLOUGHBY, KRAEMER AND SMITH . . (*Isolation of Pb*), Ind. Eng. Chem. (Anal. Ed.), 1935, 7, 33.

WITTHAUS . . *Manual of Toxicology*, London, 1911.

YOE AND HILL . (*Determination of Al*), J. Amer. Chem. Soc., 1927, 49, 2395.

YOE . . . (*Determination of Fe* (*ic*), J. Amer. Chem. Soc., 1932, 54, 4139.

NAME INDEX

PAGE
Aberhalden 152
Aubert 8
Bamberger 121
Barger 147
Barrall 63
Beam 51
Bieger 11
Bischoff 81
Bischoff 87
Briggs 5
Cavalho 113
Chamot 24
Chamot 25
Chamot 27
Chamot 144
Chamot 148
Chamot 150
Chapman 154
Charpy 7
Chavigny 61
Chavigny 63
Chevallier 109
Claps 3
Claps 124
Coleridge 135
Cornish 11
Dangl 57
Davis 118
Deniges 145
Dervieux 46
Diesselhorst 11
Dowzard 153
Dyer 155
Edgeworth-Johnstone 25
Eisler 79
Esternieder 92
Fauret 147
Favrt 3
Feigl 121
Feist 74
Finn 11
Fischer 75
Fleury 60
Forgeot 9
Forgeot 10
Frazer 92
Freak 51
Grey 12
Grey 17
Grey 18

PAGE
Gross 14
Gross 59
Guillemard 147
Guillemard 148
Gutzeit 149
Guy 5
Haberman 92
Harnack 3
Harvey 45
Heess 78
Heess 82
Heess 89
Heess 93
Herzberg 102
Herzberg 103
Herzberg 104
Hill 96
Hoffmann 80
Hoffmann 84
Hoffmann 85
Hudson 11
Hudson 12
Icard 14
Jenke 103
King 28
King 29
Landsteiner 43
Landsteiner 45
Leonard 143
Leonard 144
Lerich 124
Leung 4
Lewis 17
Lewis 79
Locard 3
Locard 7
Locard 10
Locard 14
Locard 15
Locard 34
Locard 37
Locard 50
Locard 113
Locard 124
Locard 125
Locard 129
Locard J. 98
Locard J. 99
Locard J. 100
Locard J. 148

PAGE
Lovibond 114
Lucas 35
Lucas 51
Lucas 60
Lucas 62
Lucas 63
Lucas 85
Lucas 120
Lucas 127
Lucas 138
Martley 44
Mason 24
Mason 25
Mason 27
Medinger 42
Medinger 50
Medinger 56
Metzger 78
Metzger 82
Metzger 89
Metzger 93
Metzger 114
Mitchell 5
Mitchell 7
Mitchell 74
Mitchell 79
Mitchell 81
Mitchell 87
Mitchell 92
Mitchell 97
Mitchell 93
Mitchell 98
Mitchell 101
Mitchell 113
Mitchell 114
Mitchell 118
Mitchell 121
Muller 94
Nelson 143
Nelson 144
Neumann 79
Nierenstein 75
Osborn 92
Ozorovitz 77
Ozorovitz 93
Poix 86
Poix 88

PAGE
Popp 6
Popp 14
Pregl 29
Rall 78
Rall 89
Rall 93
Rammstedt 78
Rhodes 6
Rhodes 5
Rhodes 42
Rhodes 94
Rhodes 111
Rhodes 126
Robertson 80
Robertson 84
Robertson 85
Runge 79
Schluttig 74
Scott 67
Short 150
Silbermann 77
Silvera 60
Sodermann 122
Stas-Otto 5
Stock 121
Stas-Otto 140
Stas-Otto 148
Stas-Otto 36
Still 92
Stockis 6
Strzyzowski 50
Strzyzowski 53
Taylor 119
Taylor 120
Teichmann 50
Teichmann 53
Thorpe 41
Turkel 94
Vetillard 105
Walls 119
Wall 120
Ward 81
Ward 155
Wittstein 77
Yoe 62
Zetzsche 77
Zetzche 93

SUBJECT INDEX

PAGE
Abortifacients (Identification) . 146
Absinthe 148
Adhesives (Animal) . . 122
Adhesives (Vegetable) . . 123
Apiol 148
Alkaloids (Identification) . 140
Aloes 147
Apparatus (Micro-chemical) . 21
Arsenic (Arsine) . . . 149
Arsenic (Chemico-Microscopy) 150
Arsenic (Detection) . . 148
Arsenic (Estimation) . . 152
Barrel Residue (Examination) . 61
Benzindine Reaction . . 49
Black Powder . . . 59
Bleaching Agents . . . 109
Blood (Classification) . . 43
Blood Groups . . . 43
Blood Groups (Determination) 44
Blood Test (Developments) . 45
Blood Test (Principles) . 44
Bloodstains (Examination) . 49
Bombs 67
Bombs (Composition) . . 69
Bombs (Exploded) . . 69
Bomb Fragments . . . 71
Bombs (Suspects) . . . 71
Bombs (Unexploded) . . 68
Bullets (Analysis) . . 65
Bullets (Examination) . . 65
Cellulose (Identification) . 102
Chemical Microscopy . . 20
Chemical Microscopy . . 27
Corpus Delicti . . . 49
Counterfeit Money. . . 126
Counterfeit Money (Analysis) 131
Counterfeit Money (Composition) 130
Counterfeit Money (Dusts) . 134
Counterfeit Money (Examination) 128
Decantation 23
Decantation 30
Deletion (Scoring Out) . . 110
Development. 3
Development. 4
Development (Absorption) . 6
Development (Methods) . 6
Development (Photo-chemical) 8
Development (Reagents) . 5
Development (Reduction) . 7
Distillation 29
Distillation 36
Documents (burnt) . . 118

PAGE
Documents (Date of) . . 112
Drugs (Identification) . . 145
Dust 14
Dust (Alkaloids) . . . 40
Dust (Applications) . . 27
Dust (Blood) . . . 42
Dust (Collection) . . . 15
Dust (Classification) . . 15
Dust (Distillation) . . . 35
Dust (Dyes) . . . 38
Dust (Examination) . . 17
Dusts (Extracted) . . . 16
Dust (Extraction) . . . 35
Dust (Extraction Methods) . 37
Dust (Fatty Substances) . . 38
Dust (Gome). . . . 42
Dust (Hairs) 38
Dust (Metals) . . . 42
Dust (Micro-chemical Examination) 20
Dust (Organic) . . . 35
Dust (Organic Compounds) . 38
Dust (Shellac) . . . 38
Dust (Treatment) . . . 16
Erased Text (Reconstitution) 111
Erasure (Examination) . . 108
Ergot 147
Evaporation 23
Explosions 67
Explosives (Examination) . 67
Extraction 36
Filtration 24
Filtration 28
Fingerprints (on paper) . . 5
Fingerprints (on wood) . 5
Firearms (Examination) . . 59
Florence Reaction . . 53
Forged Documents . . 106
Forgery (Addition) . . 107
Forgery (Interpolation) . 112
Forgery (Substraction) . . 107
Gamboge 147
Guaiac Resin. . . . 49
Gum (Examination) . . 122
Gunpowder (Explosion Products) 60
Gunpowder (Deposit) . . 63
Gunpowder (Iron) . . 62
Gunpowder (Potassium) . . 63
Gunpowder (Nitrates) . . 62
Gunpowder (Nitrates) . . 63
Gunpowder (Sulphates) . 62
Gunpowder (Sulphides) . 62
Gunpowder (Types) . . 59

PAGE
Gutzeit Test 153
Haematein 78
Haematoxylin . . . 78
Haemin Test . . . 50
Haemin Test . . . 51
Haemin Test (Beam) . . 51
Identification (Indirect) . . 14
Ink (Chloride Diffusion) . 14
Ink (Chloride Diffusion) . 93
Ink Colour 92
Ink (Copying power) . . 113
Ink (Ferrous iron) . . . 94
Ink Maturing . . . 91
Ink (Oxidation rate) . . 95
Ink on paper . . . 80
Ink on paper pH . . . 93
Ink solubility . . . 92
Ink (Sulphate diffusion) . 94
Inks (Aniline) . . . 80
Inks (Aniline) . . . 88
Inks (Carbonnceous) . . 80
Ink (Chemical Examination) . 81
Ink (Colouring matter) . . 79
Ink (Sulphate diffusion) . 114
Ink (Types) 74
Inks (Constitution). . . 73
Inks (Identification) . 84, 85, 86
Inks (Materials) . . . 73
Inks (Metals in) . . . 90
Inks (Micro-chemistry) . . 89
Inks (Sympathetic). . . 115
Leuco-Malachite Reaction . 50
Limit (Concentration) . . 31
Limit (Identification) . . 31
Limit (Proportion) . . 31
Logwood Ink . . . 78
Marsh Test 154
Metals (Detection) . . 17
Metals (Micro-chemical reactions) 18
Micro-chemical Equipment . 22
Micro-chemical Method (choice of) 33
Micro-chemistry . . . 28
Mugwort 148
Paper (Examination) . . 101
Paper (Loading) . . . 105
Paper (Micro-chemistry of) . 104
Paper (pigments) . . . 104
Paper (sizing) . . . 105
Paper (sizing) . . . 103
Pencil pigments . . . 97
Pencil pigments (Identification) 99
Pencil strokes (Analysis) . . 98

PAGE
Pencil writing . . . 96
Pencils (Aniline dye) . . 101
Pencils (Graphite) . . 98
Pencils (Indelible) . . 100
Poisons (Classification) . . 136
Radicles (Separation) . . 32
Reagents (Application) . . 26
Reagents (Application) . . 32
Reagents (Micro-chemical) . 21
Reinch Test . . . 151
Rue 148
Savin 147
Sealing Wax 120
Sealing Wax (Chemical Examination) 121
Skin Prints(Development) . 124
Skin Prints (On documents) . 124
Skin Prints 4
Skin Prints 3
Seminal Stains . . . 45
Smokeless Powders . . 61
Solubility 23
Sperm 53
Spot Reaction . . . 30
Stains 49
Stains (Blood) . . . 56
Stains (Candle Wax) . . 56
Stains (Classification) . . 54
Stains (Foreign Matter) . . 58
Stains (Identification) . . 54
Stains (Location) . . . 54
Stains (Paint) . . . 57
Stains (Preparations) . . 55
Starch (Dust) . . . 38
Stas-Otto (Extraction) . . 139
Strzyzowski Reaction . . 50
Sublimation 25
Sublimation 29
Sweat 3
Tannates 75
Tannates Constitution . . 77
Tannic acid 74
Teichmann's Reaction . . 50
Text (Reconstitution) . . 109
Textile Fabrics . . . 41
Tobacco Ash . . . 41
Toxic Agents . . . 135
Toxic Agents (Examination) . 138
Tracing (forgery) . . . 128
Tobacco 39
Washed Documents . . 109
Washing (chemical) . . 108
Watermarks (forged) . . 127

THE END

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